Spectroscopic and Photophysical Properties of Organoboranes and Their Transition Metal Complexes

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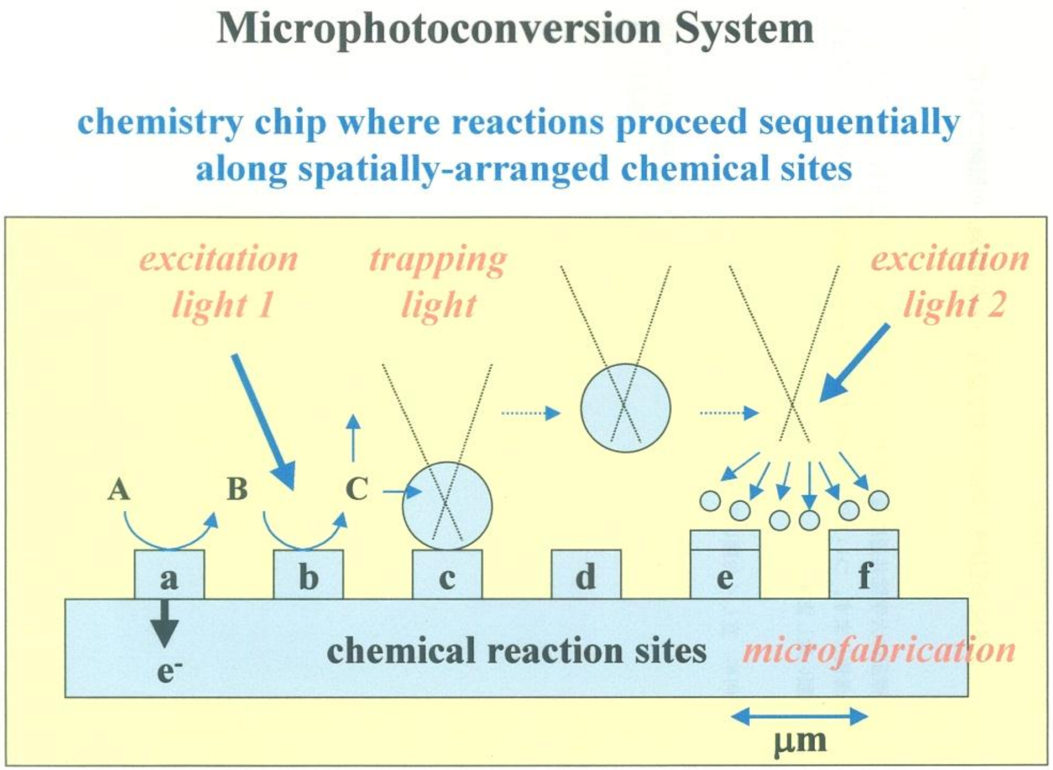
Masuhara
Microphotoconversion Project (1988 ~ 1993)

Exploratory Research for Advanced Technology: ERATO



MASUHARA Microphoto-conversion
1988~1993

Project Director:
Dr. Hiroshi Masuhara

Professor
Faculty of Engineering
Osaka University

(As of October, 1993)

Background

This project was aimed at developing innovative techniques using lasers to convert molecules and materials in the mesoscopic region by controlling various local environmental reaction conditions as a new field of micro-chemistry.

Research Results

Development of a time- and space-resolved spectroscopy: Methods were developed to observe different stages of microchemical reactions within the micrometer region. A reaction-stimulating pulsed subpicosecond (10^{-13} sec) laser combined with an observation picosecond (10^{-12} sec) laser is one example. By using a special confocal, high-resolution microscope that optically transmits UV pulsed laser light, time- and space-resolved spectroscopies were developed. Using this method, photo-relaxation processes in submicro-cubic regions can now be observed on a time scale of one to two picoseconds. A means to suppress various negative optical effects as well as time broadening of the short laser pulse (10^{-12} sec) has also been found, producing almost the ultimate time scale, since the time for one molecular orientation is also 10^{-12} sec. It has thus become possible to simultaneously satisfy the time resolution within the wavelength limitation.

Observation of dynamics in surface layers: Such elementary phenomena as electron and proton transfer as well as molecular vibration and solvation can be measured in time sequence. Although the spatial resolution of optics is limited by the wavelength, under total internal reflection the vertical resolution can be reduced from that of the wavelength by a few tens of nanometers (1/10 wavelength). By combining a picosecond laser with total internal reflection, elementary processes taking place in surface layers, thicknesses of a few tens of nanometers, have been found to be different from those of the bulk.

Holding particles by a "micrometer hand" in a strong beam: If a very strong laser beam is focused by the objective lens of a microscope, the resulting force on a particle dispersed in a liquid medium can hold it, or even many particles. Special patterns can be designed by scanning the laser beam over an area of 100 × 100 micrometers (0.1 mm) with a couple of mirrors. Within this region there are sometimes 100 particles, each comprising on the order of 10^9 molecules or atoms. Using this system, individual microparticles can be manipulated freely in three-dimensional space, characterized spectroscopically, and fabricated arbitrarily.

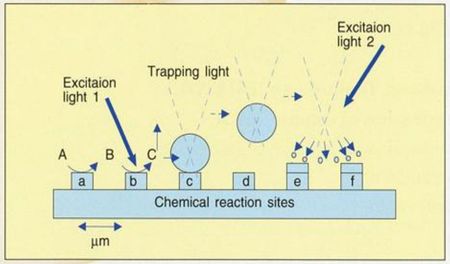
Microfabrication and microfunctionalization: Since chemical reactions are always sensitive to the surrounding environment, microphotoconversion requires small reaction sites. A selective chemical vapor deposition technique has been developed which supplies disassociated molecules to only a copper pattern on a glass or silicon substrate. Molecules can then be selectively polymerized on the micrometer pattern. A scanning electrochemical microscope was used for preparing special functionalized patterns on polymers, semiconductors, and metals. Microfabrication and microfunctionalization were also attained by photochemical reactions using a photomask and scanning electrochemical microscopy.

Micrometer size effect upon reaction dynamics: At the region of a few tens of nanometers such solvents as alcohol and water become viscous; although the molecules are always moving, on the average they are stationary. It has been shown that hydrogen bonding interactions, cluster formation, and the association/orientation of molecules are responsible for the characteristic submicrometer size effect.

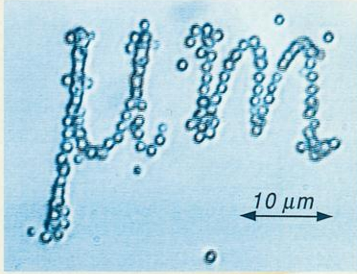
Fast response of micrometer diffusion: Even when solvent properties are completely the same as in the bulk, in a very small volume interesting phenomena are observed: for instance, every chemical phenomenon controlled by diffusion comes to completion quickly. Although in bulk chemistry step-by-step diffusion takes place, on the mesoscopic scale all reactions take place very quickly. It has been confirmed that when designing a reaction within a small volume its time scale is extremely short.

Enhancement of optical field in a microcavity: Light-lasing within a single particle has been developed, which should serve as a very convenient movable light source. This might be very useful for a photon STM; chips would not be touched, and only the laser would move. Furthermore, it has been shown that when light is confined within a small region, the light and molecules resonate so well that photochemistry becomes very efficient, leading to the molecular dynamics of a characteristic small domain.

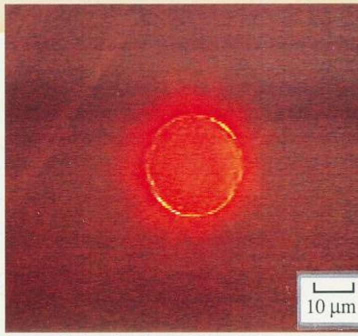
Spatial control of chemical reactions: Like in a biological cell chemical reactions should be arranged in space. In order to realize this technology, chemical relaxation sites have been established on the µm scale. By changing the distance of the reaction sites, the efficiency of chemical reactions can be highly controlled. This chemical integration of reactions will become something like a chip, not LSI, but a chemistry chip. The ideal one will require a number of steps.



A schematic diagram of Microphotoconversion system which is partially realized



Aligned polystyrene microparticles (diameter 1 µm) in ethylene glycohl



Laser oscillation of rhodamine B in a single, optically trapp poly(methyl methacrylate) microparticle in water

First Achievements in Chemistry

Time- and Space-Resolved Spectroscopies

Confocal Fluorescence Microscope

in 1988, no Japanese CFM was available and no chemist was using CFM

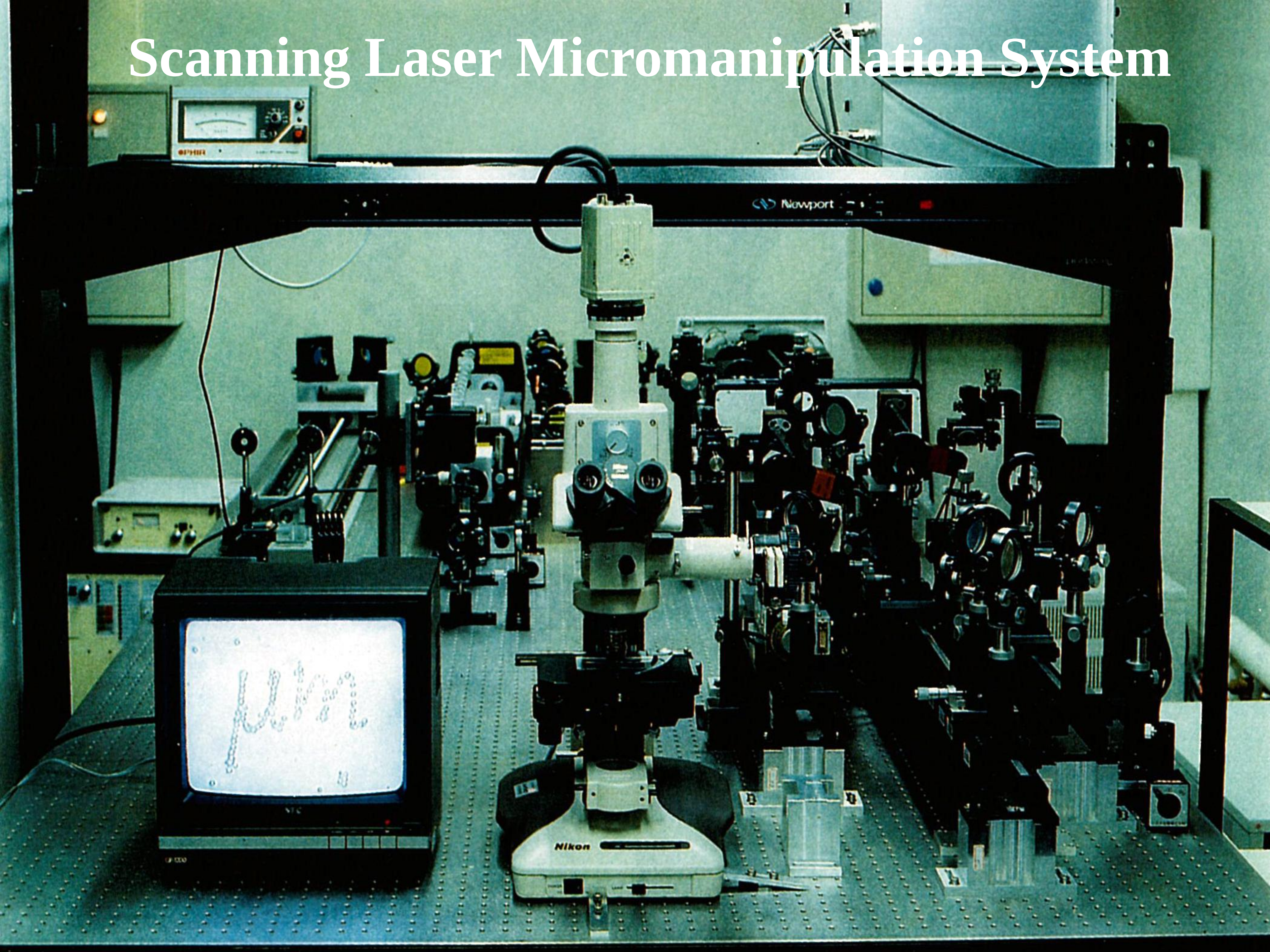
Zeiss CFM: ~36,000,000 JPY !!

fs-laser system: ~30,000,000 JPY

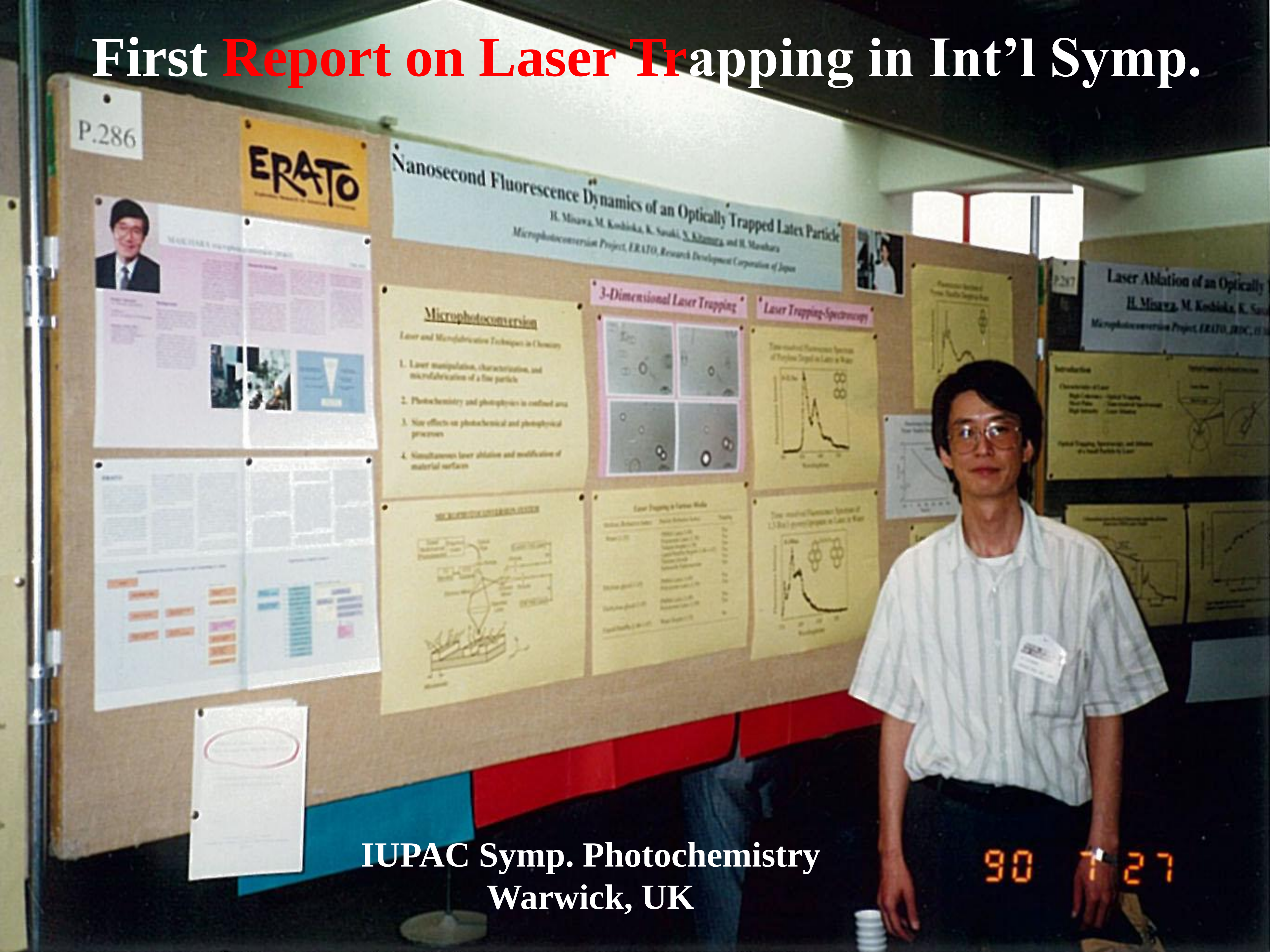
First Achievements in Chemistry

Laser Trapping

Scanning Laser Micromanipulation System



First Report on Laser Trapping in Int’l Symp.



IUPAC Symp. Photochemistry
Warwick, UK

Bell Laboratories at Holmdel, New York

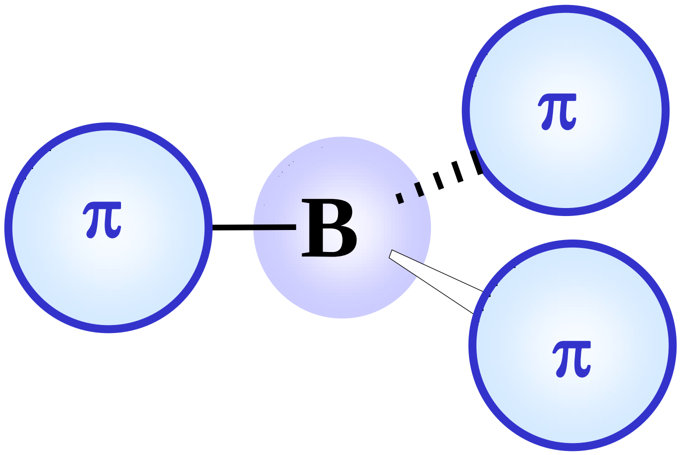
LVMH International Science Prize for Art

Optical Harmony of Microparticles in Solution

Final Symposium of the Project
Kyoto, Sep. 22, 1993

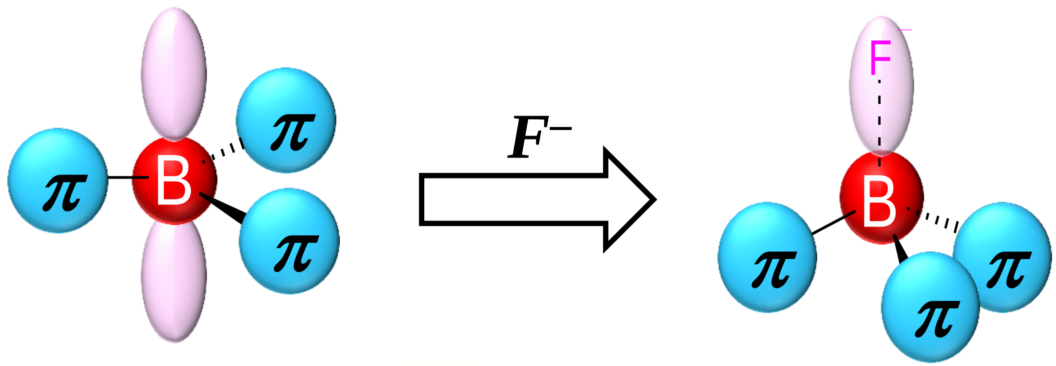
増原極微変換プロジェクト　終了シンポジウム
京都リサーチパーク　1993年９月22日

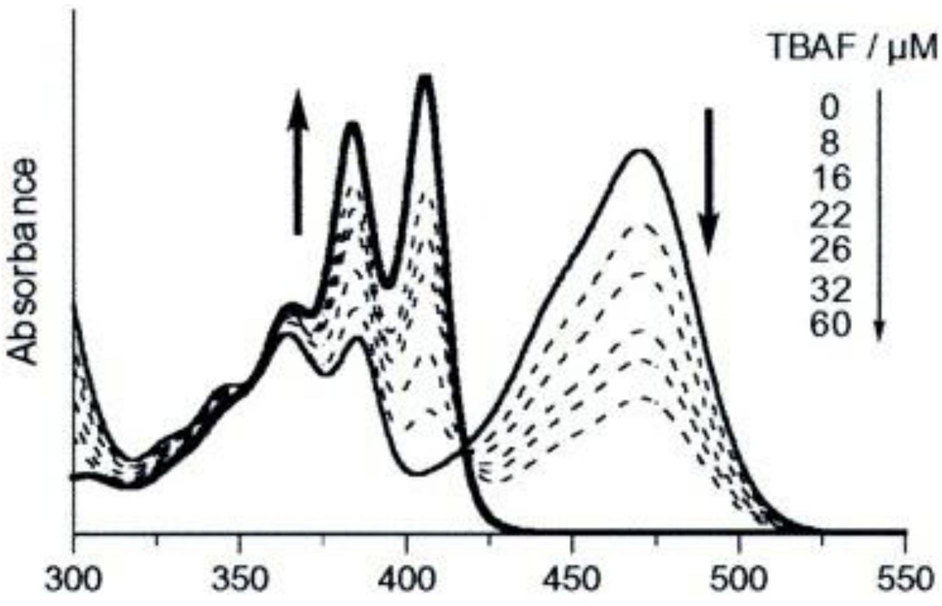
Triarylboranes



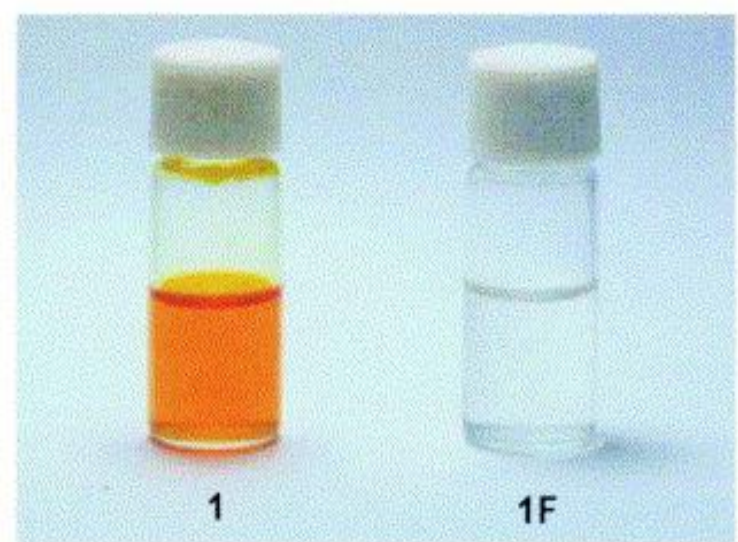
1. General Features of Spectroscopic and Photophysical Properties of Triarylboranes
2. Excited-state Dipole Moments of Triarylboranes
3. Radiative and Nonradiative Processes of Triarylboranes
4. Spectroscopic and Photophysical Properties of Transition Metal Complexes Having Triarylborane Units
5. Conclusions

Effects of Fluoride Ion





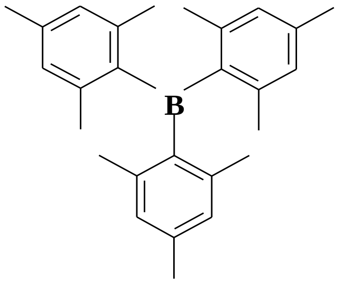
(a)



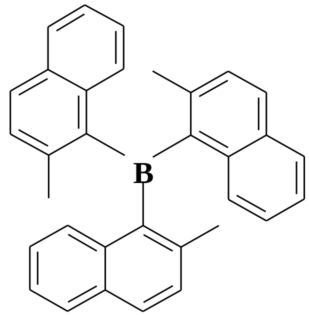
(b)

S. Yamaguchi et al. J. Orgmet. Chem. 652, 3 (2002)

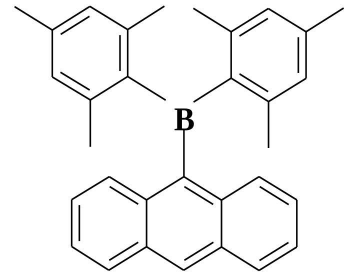
A Series of Triarylborane Derivatives



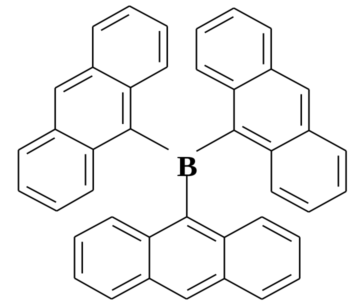
TMB



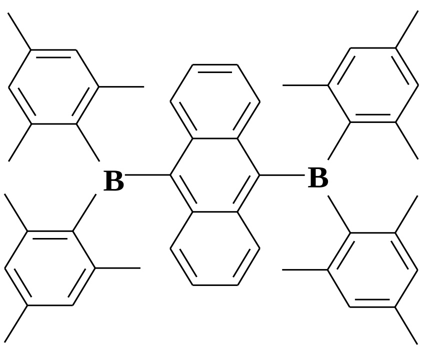
TNB



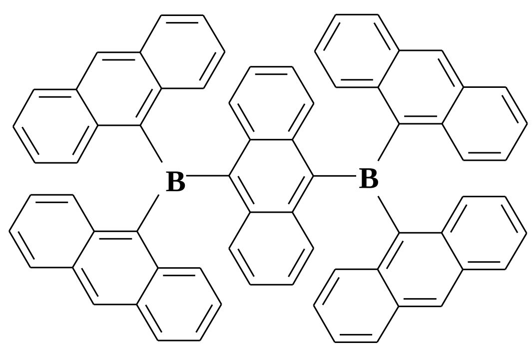
BAn(mes)$_2$



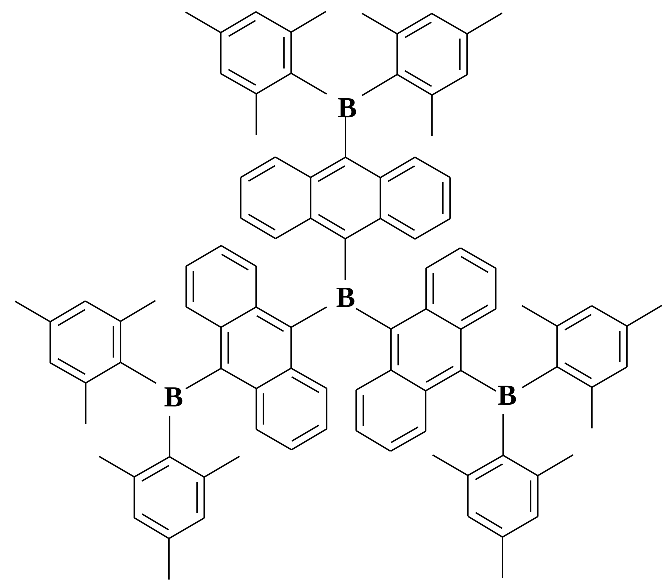
TAB



B$_2$An(mes)$_4$



B$_2$An$_5$



B$_4$An$_3$(mes)$_6$

Summary & Conclusions

1) Important roles of the π(aryl)-p(B) CT interactions in spectroscopic and photophysical properties of triarylboranes including their transition metal complexes

2) For further development of bright luminescent and photofunctonal metal complexes, the idea of synergistic MLCT–π(aryl)-p(B) interactions is of primary importance.