

JOINT STUDIES PROGRAMS

As one of the important functions of an inter-university research institution, IMS undertakes joint studies programs for which funds are available to cover research expenses as well as travel and living expenses of individuals. The proposals from domestic scientists are reviewed and controlled by an inter-university committee.

The programs are carried out under one of categories:

- (1) Joint Studies on Special Projects (a special project of significant relevance to the advancement of molecular science can be carried out by a team of several groups of scientists).
- (2) Research Symposia (a symposium on timely topics organized by collaboration between outside and IMS scientists).
- (3) Cooperative Research (a research program carried out by outside scientists with collaboration from an IMS scientist).
- (4) Use of Facility (a research program carried out by outside scientists at the research facilities of IMS except the UVSOR facility).
- (5) Invited Research Project
- (6) Joint Studies Programs Using beam lines of UVSOR Facility.
 - A. Special Projects.
 - B. Use-of UVSOR Projects.
- (7) Use of Facility Program of the Computer Center (a research program carried out by outside and inside IMS scientists at the research facilities of the Computer Center).

From October 2000, Cooperative Research Projects and Invited Research Projects for UVSOR Facility, which had belonged in the category (6), are included in the categories (3) and (4), respectively. In the fiscal year 2000, the numbers of joint studies programs accepted for the categories (1)–(5) and (7) were 3, 11, 110, 48, 5, and 156, respectively, and those accepted for subcategory (6)B was 161.

(1) Special Projects

A. Thermal and Optical Switching of Spin-Crossover Compounds

**HAYAMI, Shinya¹; MAEDA, Yonezo¹;
HOSOKOSHI, Yuko; INOUE, Katsuya; GU,
Zhongze²; SATO, Osamu²**
(¹Kyushu Univ.; ²KAST)

There has been a great interest in developing novel molecular compounds whose physical properties can be controlled by illumination. Along this line, photochemically tunable iron(II) spin-crossover complexes and a molecular photo-magnet have recently been reported. However, until now, the number of the optically switchable molecular solids reported has been quite small. This is because the strategy to achieve photo-induced switching in a solid state system is yet to be clarified. One of the requisites of optically switchable compounds is that they have nearly degenerate electronic states. Furthermore, it is known that the structural change accompanied with the switching phenomena should not be too large, because steric effects often prevent the photochemical transformation. For example, the azobenzene derivatives, which are representative photochromic molecules, do not undergo *trans*-to-*cis* photo-isomerization in the solid state due to the steric hindrance. This means that compounds with nearly degenerate electronic states and with only small structural changes occurring between the metastable state and the stable state are appropriate for optical switching. However, even if these requirements are satisfied, most never show photo-induced switching with long-lived metastable states. This is because,

although it is possible to produce a metastable state in such compounds by illumination, the metastable state rapidly relaxes back to the stable state as a result of tunneling effects due to the small structural change. Hence, in order to develop a variety of optically switchable molecular solids, strategies to prevent such a rapid relaxation from a metastable state to a ground state should be developed. We propose the introduction of strong intermolecular interactions in molecular compounds. It is thought that the cooperativity resulting from the intermolecular interaction operates to increase the activation energy for the relaxation processes, enabling the observation of a long-lived metastable state after illumination. That is, when the metastable molecular orientation reverts to the stable one, a large stress field might be built up in such compounds because of the presence of a strong binding energy between molecules.

A-1 A Novel LIESST Iron(II) Complex Exhibiting a High Relaxation Temperature

[*Inorg. Chem.* **40**, 3240 (2001)]

In the meantime a number of iron(II) compounds with long-live light-induced metastable HS states at low temperatures have been found. However, the LIESST effect has been observed only at sufficient low temperatures below 80 K so far. We directed toward to produce the compounds, which can be switched by illumination and the metastable HS state can be trapped at higher temperature. Temperature dependent spin-crossover phenomenon, $S = 0$ (LS) $\leftrightarrow$ $S = 2$ (HS) of the molecular complex, $[\text{Fe}(\text{L})(\text{CN})_2] \cdot \text{H}_2\text{O}$ (**1**) (L is Schiff-base macrocyclic ligand derived from the condensation of 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine) has been extensively studied 15 years ago by König *et al.* They have been reported that the powder

samples of complex **1** exhibited unusual magnetic behaviors, but the physical properties of single crystals and photo-induced spin transition have not been reported yet. Here, we synthesized the single crystal form of the complex **1** and also investigated its crystal structure. Moreover, we have discovered that the complex **1** exhibits LIESST effects. The relaxation temperature from the metastable HS to the original LS state is above 130 K, which is the highest temperature investigated so far.

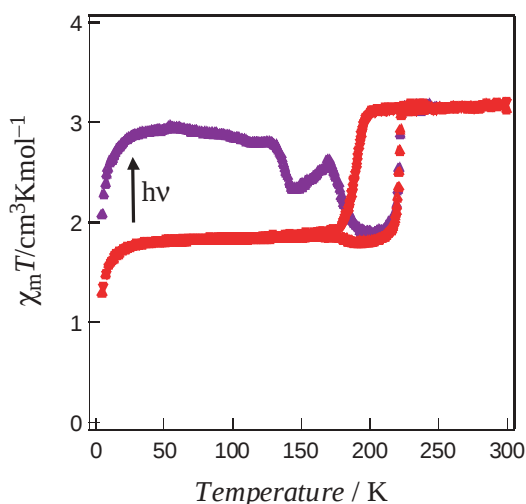


Figure 1. $\chi_m T$ vs. T plots for $[\text{Fe}(\text{L})(\text{CN})_2] \cdot \text{H}_2\text{O}$ before and after illumination at 550 nm.

A-2 Pressure-Stabilized Low-Spin State for Binuclear Iron(III) Spin-Crossover Compounds

[*Bull. Chem. Soc. Jpn.* in press]

Binuclear iron(III) spin-crossover complexes with salen ligand $[\text{Fe}_2(\text{salen})_2(\text{L})](\text{BPh}_4)_2$ were synthesized and characterized by single-crystal X-ray diffraction, Mössbauer spectra, magnetic susceptibilities and electronic spectra, where H_2salen is a pentadentate ligand derived from salicylaldehyde and 3,3'-diaminodipropylamine and L is a didentate axial ligand (az = azobis(4-pyridine) and cc = 4,4'-vinylenebis(pyridine)). The structures of $[\text{Fe}_2(\text{salen})_2(\text{az})](\text{BPh}_4)_2$ (**1**) and $[\text{Fe}_2(\text{salen})_2(\text{cc})](\text{BPh}_4)_2$ (**2**) were determined at both 100 K and 298 K. The complexes **1** and **2** exhibited the spin-crossover behavior depending on temperature within the temperature range of 200 to 350 K, and rapid spin equilibrium behavior was observed by means of Mössbauer spectroscopy at 293 K. The complexes **1** and **2** also exhibited a pressure-induced spin transition between the rapid spin equilibrium state and low-spin state at 300 K. Such a pressure-induced spin transition has not been reported earlier.

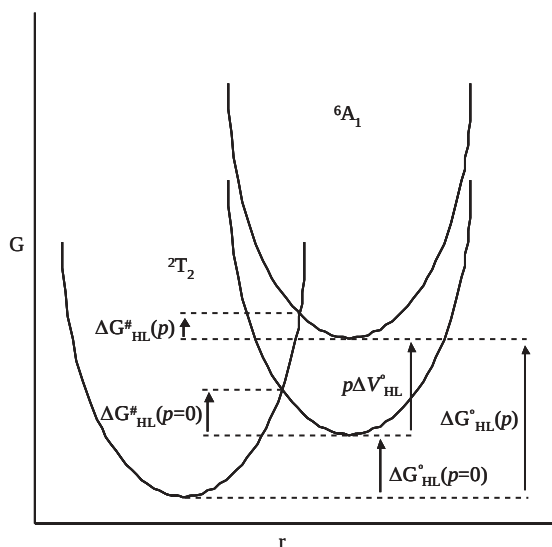


Figure 1. Schematic representation of the influence of pressure on the low-spin state (2T_2) and high-spin state (6A_1). Pressure increases the zero point energy difference, $\Delta G^\circ_{\text{HL}}(p)$ by the work term $p\Delta V^\circ_{\text{HL}}$ and decreases the activation energy $\Delta G^\ddagger_{\text{HL}}(p)$, thus favouring the low-spin state and increasing the rate constant k_{HL} .

A-3 Iron(III) Spin-Crossover Compounds with a Wide Apparent Thermal Hysteresis at around Room Temperature

[*J. Am. Chem. Soc.* in press]

The magnetic properties of the spin-crossover compounds, $[\text{Fe}(\text{qsal})_2]\text{NCSe} \cdot \text{MeOH}$ (**1**) and $[\text{Fe}(\text{qsal})_2]\text{NCSe} \cdot \text{CH}_2\text{Cl}_2$ (**2**), have been measured. We have discovered that both compounds **1** and **2** have exhibited a wide thermal hysteresis loop of 140 K ($T_{1/2}^\uparrow = 352$ K and $T_{1/2}^\downarrow = 212$ K) and 180 K ($T_{1/2}^\uparrow = 392$ K and $T_{1/2}^\downarrow = 212$ K) respectively in the first cycle. Thermogravimetric analysis shows that solvent molecules escape from compounds **1** and **2** at around 340 K and 395 K, respectively. This means that the hysteresis loops observed for the first cycle are only apparent ones. Following the first loop, they show a two-step spin crossover in warming mode. The so-called "step 1" and "step 2" are centred around $T_{1/2(\text{S1})}^\uparrow = 215$ K and $T_{1/2(\text{S2})}^\uparrow = 282$ K, respectively. On the other hand, it shows a one-step spin crossover at $T_{1/2}^\downarrow = 212$ K in cooling mode. The hysteresis widths can be estimated to be 3 K (step 1) and 70 K (step 2), assuming that the widths in "step 1" and "step 2" are defined as the difference of $T_{1/2(\text{S1})}^\uparrow$ and $T_{1/2}^\downarrow$, and $T_{1/2(\text{S2})}^\uparrow$ and $T_{1/2}^\downarrow$, respectively. The hysteresis width of 70 K in "step 2" is one of the widest values reported so far for spin-crossover complexes. It is thought that the cooperativity operating in the complexes mainly arises from the intermolecular π interactions between quinoline and phenyl rings. Using the model reported by Kahn and Real *et al.* we are able to simulate the hysteresis loop with a two-step spin-crossover in warming mode and a one-step transition in cooling mode.

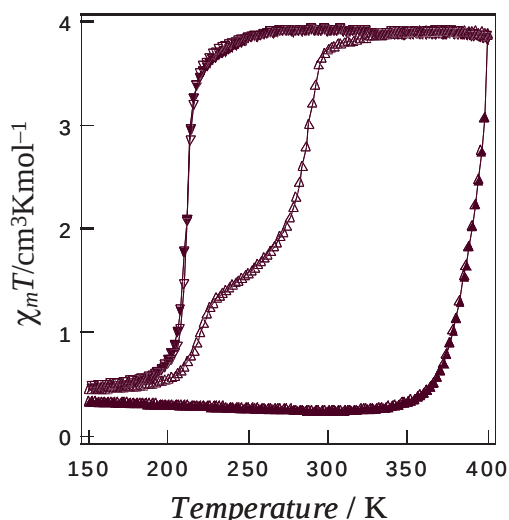


Figure 1. $\chi_m T$ versus T plots for **2**. The sample was warmed from 5 K to 400 K (▲) and then cooled from 400 K to 5 K (▼) in the first cycle, and the sample was warmed from 5 K to 400 K (△) and then cooled from 400 K to 5 K (▽) in the second cycle at a rate of 2 K min⁻¹.

B. Photoinduced Energy Transfer in Meso-Acridine-Porphyrins

TANAKA, Yasutaka¹; MATSUEDA, Satoshi¹;
YAMASHITA, Yoshinori¹; SUZUKI, Hiroshi¹;
ISHIDA, Akito²

(¹Shizuoka Univ.; ²Kyoto Pref. Univ.)

Outline of the project:

Combination of several types of chromophores possessing distinct physical properties such as absorption coefficients and wavelengths leads to a valid light harvesting system with a broader absorption band and is thus attracting considerable attentions. In nature the light-harvesting complexes in photosynthetic systems consist of a few kinds of pigment molecules involving porphyrins and carotenoids and enable them to absorb and collect the solar energy comprised of many wavelengths where the intermolecular energy transfer between the pigments plays a central role in delocalizing and stabilizing the energy collected. In addition the spatial arrangement of the pigments affects the transfer efficiency in a striking manner. The importance and complexity of energy as well as electron transfer in nature have led many researchers to look into simplified model systems composed of donor and acceptor molecules for studying the fundamental process of energy and electron transfer and for constructing artificial photosynthetic systems capable of capturing and storing solar energy. We propose and design novel chemical structures of porphyrin molecules directly bound to an acridine ring(s) as a multichromophoric molecule. Acridine and porphyrin are both pigment possessing independent absorption coefficients and wavelengths. One may expect that a combination of these pigment lead to chromophores involving the physical properties derived from original molecules as well as an acquired property from the combination. Here the efficiency of the light harvesting and energy transfer in the acridine-porphyrins is

explained in terms of the spatial arrangement of the chromophores in ground and excited states.

Summary:

Multichromophoric molecules constituted of acridine and porphyrin moieties that are directly bound through covalent bonds were newly synthesized. Meso-monoacridinylporphyrin (**3**) and 5,15-bisacridinylporphyrin (**1**) exhibited that the fluorescence of the acridine chromophore was completely quenched by covalently bound porphyrin indicating the effective energy transfer from acridine to porphyrin. In contrast 5,10-bisacridinylporphyrin (**2**) emits the fluorescence of both acridine and porphyrin when irradiated with light of acridine absorption showing partial energy transfer. The definitive discrepancy in the energy transfer behavior in acridine-porphyrins is expounded by mean of the dipole-dipole mechanism.

B-1 Syntheses of Acridine-Porphyrins

Acid catalyzed condensation of dipyrromethane (**5**) with 9-formylacridine (**6**), followed by oxidation using DDQ gave **1** as the prospective **2** (**5**) + **2** (**6**) condensation product along with porphyrins of **2**, **3**, and **4** (Figure 1). The unforeseen formation of these three porphyrins resulted from the scrambling (migration and loss) of meso-substituents. The scrambling occurred when the meso-substituents were bulky enough to unstabilize a porphyrinogen as a porphyrin precursor which is thus ultimately oxidized to give corresponding porphyrin. The porphyrin syntheses from 9-anthraldehyde and 1-naphthaldehyde with pyrrole were reported: the former fails (0%) and the latter succeeded (52%) although the two aldehydes possessed similar structures. Molecular model studies of the porphyrinogen molecules indicated that the anthracene 1-H is thrust into a severe eclipsing interaction with the *meso* hydrogen while the 8-H is unobstructed in the lower groove when 9-anthraldehyde or 9-formylacridine were adopted as aldehyde (Figure 2(a)). Naphthaldehyde can avoid the meso hydrogen eclipsing interaction by rotation of the 8-H into the lower groove (Figure 2(b)). These are causes of the formation of the meso-substituents scrambling products as well as of the low yields. The structures of the porphyrins synthesized here were characterized by mean of ¹H, ¹³C, and 2D (¹H-¹H COSY and NOESY, ¹H-¹³C COSY) NMR spectra and mass spectroscopy.

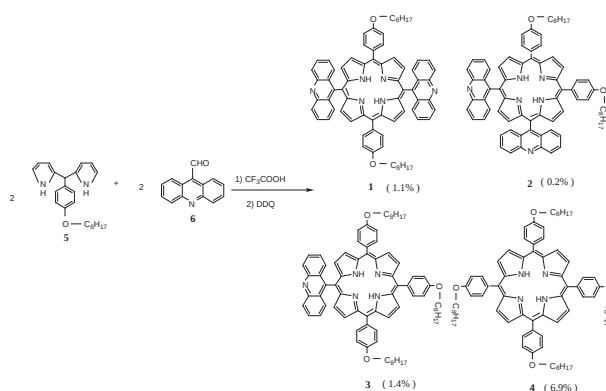


Figure 1. Synthesis of Acridine-Porphyrins.

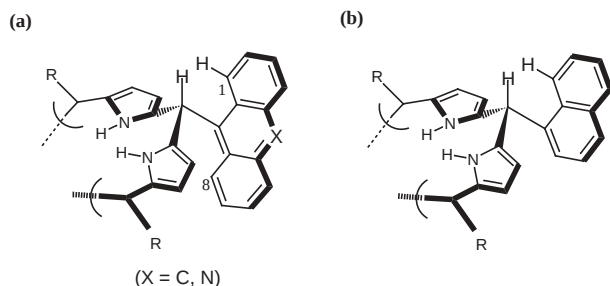


Figure 2. Steric structures of porphyrinogues possessing the meso-substituent of (a) 9-anthranyl or acridin-9-yl and (b) 1-naphthyl.

B-2 Photoinduced Intramolecular Energy Transfer from Acridine to Porphyrin

Acridine-porphyrins (**1**, **2**, and **3**) closely resembled each other in their absorption spectra (Figure 1) except that the acridine absorption intensity (254 nm) in **1** and **2** is approximately double of that in **3** due to the number of acridine rings attached to porphyrin (B-1 Figure 1). The slight or no wavelength shifts in the Soret (426 nm) and acridine absorption (254 nm) bands in acridine-porphyrins from the absorptions of parent porphyrin (**4**, $\lambda_{\text{max}} = 424$ nm) and acridine (254 nm) suggested slight or no electronic interactions between the intramolecular chromophores. In particular PM3 semi-empirical calculation indicated that the acridine and porphyrin rings are almost orthogonal to one another in their energy minimized structures where the overlap of molecular orbitals of the chromophores thus seem to be scarce in the ground state (Figure 2).

When meso-tetraphenylporphyrin (TPP) was mixed with acridine in the ratio of 1:1 or 1:2 in CHCl_3 the fluorescence of acridine (broad luminescence at about 400 nm) was barely quenched by coexisting porphyrin indicating difficulty in transferring energy. In contrast **1** fluoresces light at 653 nm, the porphyrin fluorescence, without emitting the acridine fluorescence upon irradiation with light at 254 nm (Figure 3). **3** also fluoresces light at 653 nm with scanty fluorescence of acridine itself (Figure 4). These are clearly showing that the energy transfer between covalently bound chromophores efficiently takes place. The fluorescence life time measurements also proven the energy transfer. Two kinds of decay curves possessing respective rate constants were found in **3** on illumination at 250 nm and observation of the emission at larger than 300 nm (Figure 5(a)), the fluorescence life time of 10.7 ns being attributed to porphyrin and that of 1.8 ns being to acridine. In particular when irradiated at Soret band at 420 nm and observed the emission at larger than 600 nm the only life time afforded was to be 9.3 ns (Figure 5(b)), which is almost identical with that of the porphyrin fluorescence observed above. In marked contrast to **1** **2** emits light of both acridine and porphyrin fluorescence along with the decrease of the porphyrin fluorescence intensity as compared with those in **1** and **3** (Figure 6). This exhibits that the only partial energy transfer from acridine to porphyrin is occurring in **2** although **1** and **2** contain the same numbers of acridine and porphyrin rings in their structures.

The energy migrates from the excited to ground state

molecules when their orientation, distance, energy levels, and the other conditions is profitable to transfer. The inter- or intramolecular energy transfer is based on interacting transition dipole moments in energy donor and acceptor moieties in the dipole-dipole mechanism. Since the acridine fluorescence band gives a much greater overlap with the Soret band the intramolecular energy transfer in **1**, **2**, and **3** should be driven by this mechanism. Thus the orientation of the acridine and porphyrin rings might be almost coplanar to one another in the excited state so as to induce the energy transfer. The molecular model studies including the PM3 calculation and CPK model exhibited that the two rings are capable of rotating along the C-C bond axis between the porphyrin meso and acridine 9 positions until the protons in the b in pyrrole and acridine 1- or 8-positions come into contact, where the two rings are nearly coplanar. The two chromophores in **1** and **3** seem to be able to adopt this orientation (Figure 7(a)) while those in **2** seem to be unable to do it due to a severe eclipsing interaction of an acridine 2- or 7-H with the adjacent acridene 2- or 7-H by rotation of the respective acridine rings (Figure 7(b)). Eventually the photo-excited acridine in **2** was deactivated by emitting the acridine fluorescence before the energy is migrating to porphyrin.

This is a quite unique example of an intramolecular energy transfer system since the definitive discrepancy in the energy transfer efficiency is derived only from the position of the acridine substituent in acridine-porphyrins, thus 5,15-bisacridinyl (**1**) or 5,10-bisacridinyl (**2**). We are about to measure the fluorescence life time for **1** and **2** in order that we gain a further insight into nature of novel synthesized porphyrins.

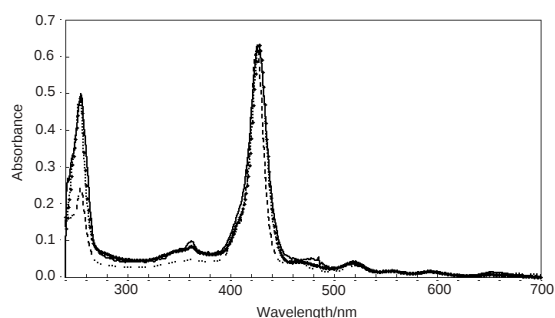


Figure 1. Absorption spectra of **1** (solid line), **2** (dotted line), and **3** (dashed line) in CHCl_3 .

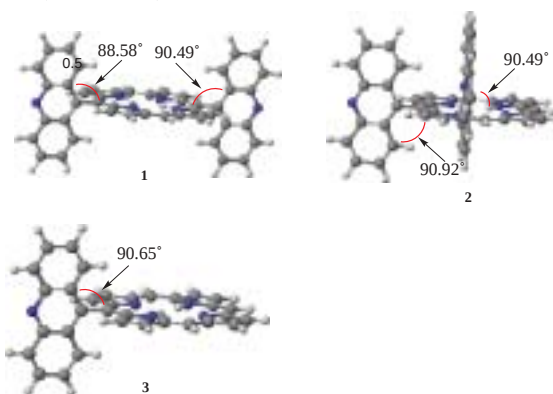


Figure 2. Energy minimized structures of **1**, **2**, and **3** calculated by PM3.

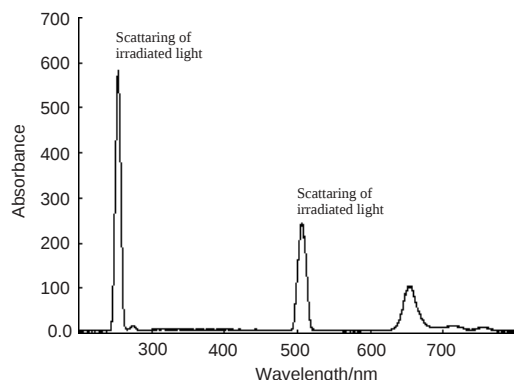


Figure 3. Fluorescence spectrum of **1** in CH_2Cl_2 (excited at 254 nm).

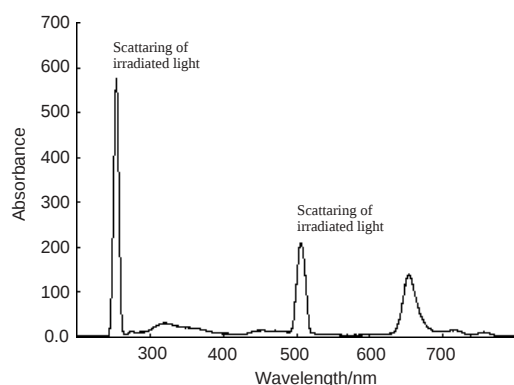


Figure 4. Fluorescence spectrum of **3** in CH_2Cl_2 (excited at 254 nm).

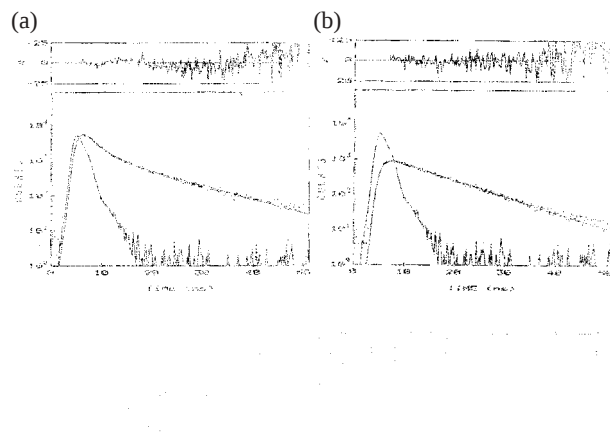


Figure 5. Time-resolved fluorescence intensity of **3** in CH_2Cl_2 , (a) EX 250 nm, EM > 300 nm, (b) EX 420 nm, EM > 600 nm.

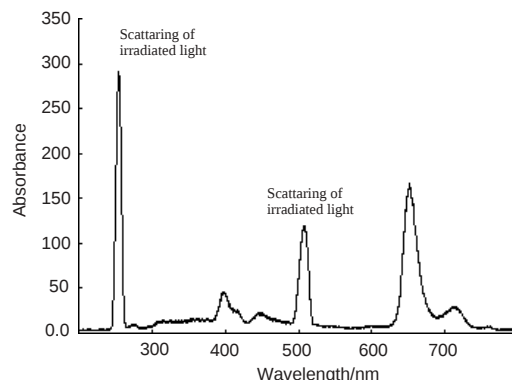


Figure 6. Fluorescence spectrum of **2** in CH_2Cl_2 (excited at 254 nm).

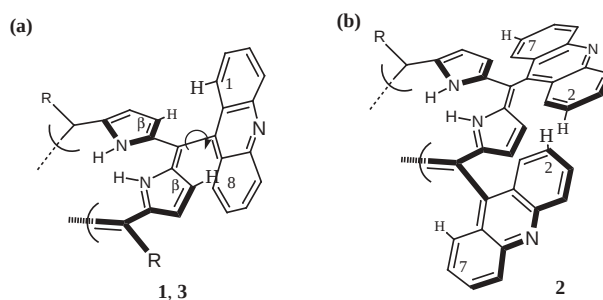


Figure 7. Steric structures of acridine-porphyrins of (a) **1** and (b) **2**.

(2) Research Symposia

(from September 2000 to August 2001)

- Chemistry in Intense Laser Fields
(September 4-5, 2000)
Chair: **YAMAUCHI, Kaoru**
- Present Status of VUV Light Sources and Its Application
(September 17-19, 2000)
Chair: **KUROSAWA, Kou**
- Present Status and Future Trends of Fullerene Chemistry and Physics
(November 23-25, 2000)
Chair: **KOBAYASHI, Kaoru**
- Future Prospect of Nano-Science by Electron Microscope
(November 21-22, 2000)
Chair: **TANAKA, Nobuo**
- Molecular Science on Protein Dynamics: Toward Understanding of Fluctuation
(December 25-27, 2000)
Chair: **MIZUTANI, Yasuhisa**
- Recent progress in functional organic molecules -- design, synthesis and physical properties
(January 18-20 2001)
Chair: **HOSOKOSHI, Yuko**
- New Needs in the UV and VUV Region for

Synchrotron Radiation Application
(December 11-12)

Chair: **FUKUI, Toshikazu**

8. Application of VUV and SX Pulses and Future Prospect
(January 26-27, 2001)
Chair: **KAMATA, Masao**
9. Symposium on Physical Chemistry for Young Researcher of Molecular Science
(June 12, 2001)
Chair: **SHIBUYA, Kazuhiko**
10. Solution Chemistry in the 21st Century:
A Perspective from the Molecular Science
(May 31- June 2, 2001)
Chair: **SATO, Hirofumi**
11. What kind of universality is present in functional mechanisms of proteins?
(July 17-18, 2001)
Chair: **MORIMOTO, Hideki**

(3) Cooperative Research

This is one of the most important categories that IMS undertakes for conducting its own research of the common interest to both outside and IMS scientists by using the facilities at IMS. During the first half of the fiscal year of 2000 ending on September 30, 61 outside scientists jointed Cooperative Research programs and during the second half, 49 outside scientists did. The names and affiliations of those collaborations are found in Research Activities.

(4) Use of Facility

The numbers of projects accepted for the Use-of-Facility program during the first half and the second half of the fiscal year of 2000 amounted to 3 and 2 for the Laser Research Center for Molecular Science, 21 and 20 for the Research Center for Molecular Materials, and 1 and 1 for Equipment Development Center, respectively.

(5) Invited Research

Under this joint-study program, several scientists were invited from other institutions of help for construction and improvement of instruments in IMS. The total number of the projects in this category was 5 (2 for the first half and 3 for the second half) in the fiscal year of 2000.

(6) UVSOR

In the UVSOR Facility with the 750 MeV electron storage ring, there are twenty beam lines available for synchrotron radiation research (see UVSOR ACTIVITY REPORT 2000). The Experimental facility of each beam line is also described in this report. Under the following programs, many users outside and inside IMS have carried out a number of synchrotron radiation studies: A. Special Projects. B. Use-of UVSOR Projects.

A. Special Projects

B. Use-of UVSOR Projects

Under this joint-study program, many synchrotron radiation experiments have been carried out with the beam lines of in-house staff in cooperation with scientists who were invited from other institutions. The total number of the projects in this category was 161 (86 for the first half and 75 for the second half) in the fiscal year of 2000.

(7) Use of Facility Program of the Computer Center

The number of projects accepted for the Use-of-Facility program of the Computer Center during the fiscal year of 2000 amounted to 156 (635 user) and computer time spent for these projects 143343 hours (converted to the IBM SP2 time), and amounted to 82% of the total annual CPU time used.