



|              |                                                                                       |
|--------------|---------------------------------------------------------------------------------------|
| Title        | MOLECULAR ASSEMBLIES OF PORPHYRINS ON GOLD SURFACE AND THEIR PHOTOPHYSICAL PROPERTIES |
| Author(s)    | 秋山, 毅                                                                                 |
| Citation     | 大阪大学, 1997, 博士論文                                                                      |
| Version Type | VoR                                                                                   |
| URL          | <a href="https://doi.org/10.11501/3129003">https://doi.org/10.11501/3129003</a>       |
| rights       |                                                                                       |
| Note         |                                                                                       |

*The University of Osaka Institutional Knowledge Archive : OUKA*

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

# **MOLECULAR ASSEMBLIES OF PORPHYRINS ON GOLD SURFACE AND THEIR PHOTOPHYSICAL PROPERTIES**

**TSUYOSHI AKIYAMA**

Department of Applied Fine Chemistry

Faculty of Engineering

Osaka University

1997

# MOLECULAR ASSEMBLIES OF PORPHYRINS ON GOLD SURFACE AND THEIR PHOTOPHYSICAL PROPERTIES

(ポルフィリン類の金表面への分子集合体形成とその光物性)

TSUYOSHI AKIYAMA

Department of Applied Fine Chemistry  
Faculty of Engineering  
Osaka University  
1997

# Preface

This study was carried out under the direction of Professor Yoshiteru Sakata at the Institute of Scientific and Industrial Research, Osaka University, Japan, from 1992 to 1997. The interest of this study is focused on development of novel light energy conversion system, which mimics photosynthetic electron transfer.

The author wishes to express his sincere gratitude to Professor Yoshiteru Sakata for giving a chance to study on this field, kind guidance, helpful suggestion, and continuous encouragement throughout this work. The author is also deeply grateful to Dr. Hiroshi Imahori for his continuous advice, stimulating discussions, and hearty encouragement.

He also acknowledges Associate Professor Takahiro Kaneda, Dr. Ken-ichi Sugiura, and Technical Official Chiaki Takehisa for their encouragement, helpful suggestions, and supporting this research.

The author is also grateful to Professor Shin-ichiro Suzuki, Professor Hiroshi Iwasaki, Professor Masao Kaneko, Professor Taku Matsuo, Professor Sunao Yamada, Professor Tadashi Okada, Dr. Tasuo Yoshinobu, Dr. Motoi Nakao, Dr. Hiroaki Yonemura, Dr. Yasuro Niidome, Dr. Kiminori Ushida, Dr. Masao Takahashi, Dr. Masahiro Shirakawa, Mr. Akira Shiga, Mr. Masato Hasegawa, Mr. Seiji Taniguchi, Mr. Takanori Tanaka, Mr. Yoshiyuki Okuda, and Mr. Tadachika Nakayama for helpful suggestions, contribution of each measurement, teaching techniques of using a device for special measurement and making electrodes and useful discussion.

Special thanks are given to all the members of Sakata lab. especially Dr. Hirohito Tsue, Mr. Eiichi Yoshizawa, Mr. Masanori Aoki, Mr. Kohji Yamada, Mr. Anawat Ajawakom, Mr. Takayuki Azuma for their supporting his research.

Furthermore, the author thanks all friends of him.

Finally, the author would like to express his thanks to his parents and brother for their understanding and hearty encouragement.

Osaka, Japan

January, 1997

Tsuyoshi Akiyama

# Contents

|                |       |
|----------------|-------|
| <b>Preface</b> | ... 2 |
|----------------|-------|

|                             |       |
|-----------------------------|-------|
| <b>General Introduction</b> | ... 6 |
|-----------------------------|-------|

## **1. Preparation of Molecular Assemblies of Porphyrin-Linked Alkanethiol on Gold Surface and Their Redox Properties**

|                            |        |
|----------------------------|--------|
| 1.1 Introduction           | ... 8  |
| 1.2 Experimental Section   | ... 8  |
| 1.3 Results and Discussion | ... 9  |
| 1.4 Conclusion             | ... 10 |
| 1.5 Synthesis              | ... 10 |
| 1.6 Referenece             | ... 12 |

## **2. Synthesis and Self-Assembly of Porphyrin-linked Fullerene on Gold Surface Using S-Au Linkage**

|                            |        |
|----------------------------|--------|
| 2.1 Introduction           | ... 14 |
| 2.2 Experimental           | ... 15 |
| 2.3 Results and Discussion | ... 15 |
| 2.4 Conclusion             | ... 19 |
| 2.5 Synthesis              | ... 19 |
| 2.6 Reference              | ... 24 |

|                                     |        |
|-------------------------------------|--------|
| <b>Figures, Tables, and Schemes</b> | ... 25 |
| <b>Conclusion</b>                   | ... 61 |
| <b>Publications</b>                 | ... 62 |

# General Introduction

Recently much utilization of solar energy has been studied extensively relevant to environmental and energy problems. Since, solar energy exists infinitely and does not pollute the environment, it is expected to become more important compared with other energy sources. Until now, many studies on inorganic solar cells using semiconductors have been conducted, and some of them have already been commercially available. Organic solar cells have been paid much attention in relation to photosynthesis. The key reaction in photosynthesis is photoinduced charge separation consisting of multistep electron transfer processes. X-ray structure analysis of purple bacterium, reported by Deisenhofer et. al. in 1984, shows how well each chromophore is incorporated in reaction center matrix. Such special arrangement of chromophores ensures efficient multistep ET processes in high quantum yield, which eventually convert the light into chemical energy. To elucidate the controlling factors in photosynthetic ET, many donor-acceptor molecules have been prepared. Evaluation of these model compounds in ET has revealed the factors governing rates of ET reactions including driving forces, distances and orientations, the nature of intervening medium, and solvent. Some of these well-defined models, such as triad, tetrad, and pentad have displayed long-lived charge separated states with high quantum yield. Although this success has enabled us to control reaction mode as well as efficiency of CS in donor-acceptor linked molecules. There is still a fundamental problem to be solved for application of these molecules in light energy conversion system: How can we orient and arrange these molecules unidirectionally? A variety of methods have been utilized, to assemble fundamental molecules such as, Langmuir-Blodgett films, bilayers, polymers, micelles, and vesicles and so on. However, these methods have disadvantages in stability and regularity. The self-assembled monolayer technique was introduced during the last decade. It enables the molecules of interest to be bound chemically on the surface like metals, semiconductors, and insulators in a highly organized and less defective manner. Especially, sulfur compounds (thiols, disulfides, and sulfides) bind to gold tightly to form highly-oriented and stable monolayers. There have been many reports about the modified electrode with redox active molecules



using self-assembling method. Therefore, this film seems to be the most promising approach for realizing photovoltaic devices at the nano-scale level. I have applied this technique to single molecule as well as donor-acceptor linked molecules and have developed supramolecular assembly of these molecules on gold surface. Such systems are expected to mimic photoinduced CS events in photosynthesis.

In chapter 1, synthesis and molecular assembly of porphyrin dimers containing disulfide bond in a spacer are described.

In chapter 2, synthesis and molecular assembly of porphyrin-linked fullerenes molecules are presented.

# 1

## Preparation of Molecular Assemblies of Porphyrin-Linked Alkanethiol on Gold Surface and Their Redox Properties

### 1.1 Introduction

As the first stage for construction of photovoltaic device self-assembled monolayers techniques was applied to porphyrins since they are frequently employed as donor/acceptor as well as sensitizer in model compounds for photosynthetic ET. It is well known that porphyrins bearing thiol group are susceptible to being oxidized by light or dioxygen. Considering that disulfide group is similar to thiol groups in formation of SAM on gold surface, porphyrin dimer with a alkyl spacer containing disulfide group seems to be suitable for supramolecular assembly of the porphyrin on gold (Fig. 1). There is some controlling factors to obtain the SAM in highly regular manner. Thus, Van der Waals interaction between alkyl chains as well as  $\pi$ - $\pi$  interaction between porphyrin chromophores are crucial for desirable supramolecular structure. Such SAM provides a new approach to model systems as function as light antenna complexes in photosynthesis, where chlorophylls and carotenoids collectors.

### 1.2 Experimental Section

The synthesis of disulfides **4** and **5** was carried out as shown in Scheme 1. The coupling reaction of **2** and **3** using 6-chloro-2,4-dimethoxy-1,3,5-triazine (CDMT) and purification by preparative gel permeation chromatography with  $\text{CHCl}_3$  gave **4** in 53% yield. Preparation of zinc complex **5** was carried out by treatment of **4** with zinc acetate in dichloromethane-methanol. Structures of all new compounds were confirmed mainly spectroscopic analysis. An gold electrode with smooth surface was obtained by vacuum deposition of gold on Pyrex(R) plate (Fig. 2). An gold electrode with (111) surface was purchased from SHIBAO was used for photocurrent measurement. This electrode was prepared by vacuum deposition of gold

(2000Å) on Cr layer (50Å) on Si (100) wafer (SUMITOMO SITX CORP) (Fig. 3). The porphyrin molecules were deposited on the gold surface by soaking the electrode in 0.5mM  $\text{CH}_2\text{Cl}_2$  solution of **4** or **5** for 24hr, washed well with enough amount of  $\text{CH}_2\text{Cl}_2$  and dried with a stream of  $\text{N}_2$  (Fig. 4). Electrochemical cell for all measurement was shown in Fig. 5.

## 1.3 Results and Discussion

### Fluorescence Emission Spectra

Fluorescence emission spectra of **4** / Au and **5** / Au were shown in Fig. 6. The fluorescence maxima of **4** / Au (655 nm, 720 nm) and **5** / Au (609 nm, 650 nm) are quite close to those of **4** / Pyrex and **5** / Pyrex, respectively, indicating that the porphyrin chromophore is immobilized on the electrode surface. It should be noted here that relative intensities of  $\alpha$  and  $\beta$  bands in **4** / Au and **5** / Au are considerably different from those in solution. These indicate that electronic states of the porphyrins on the Au surface are significantly varied.

### X-ray photoelectron spectroscopy (XPS)

Photoelectron binding energies of **4** / Au and **5** / Au measured by XPS were summarized in Table 1. The peaks of C(1s), O(1s), and N(1s) suggest the existence of porphyrin rings in **4** / Au and **5** / Au. Furthermore, the peaks due to S(2p<sub>3/2</sub>) energies were observed for **4** / Au and **5** / Au, respectively. These values (**4** / Au : 162.1 eV, **5** / Au : 162.2 eV) are in good agreement with the reported values of S(2p<sub>3/2</sub>) (161.9 eV, 161.8 eV) to thiolate bound to gold. This results clearly indicate that porphyrins are immobilized on gold surface with a S-Au bond.

### Electrochemical measurement

Figure 7 shows cyclic voltammograms of **4** / Au, **5** / Au, and bare gold electrode as a reference. In **4** / Au and **5** / Au oxidative waves due to porphyrin moieties were seen, while no apparent reductive peaks due to the porphyrins were observed because of the cleavage in **5** / Au (834 mV, 1225 mV) can be assigned to the first and second oxidative potentials of zincporphyrin moiety by comparing those for **5** in  $\text{CH}_2\text{Cl}_2$  (803 mV, 1124 mV). It should be noted here that the peak splitting between the foreground and back waves are unusually large. It may be ascribed to the relating slow ET between the elec-

trode and the porphyrin or counter anion for the porphyrin. Number of the adsorbed molecules for **5** / Au was estimated to be  $5.9 \times 10^{-11}$  mol / cm<sup>2</sup>. Weak irreversible wave from the porphyrin was detected for **4** / Au. This may be due to irregular structure of the SAM on gold surface.

#### Photocurrent measurement

The modified electrode was irradiated with 150W Xenon lamp. The result of photocurrent measurement was showed in Figure 8. A large cathodic photocurrent using **4** / Au as a modified electrode was clearly seen at negative potentials at around -200 mV (vs. Ag / AgCl) in the presence of methylviologen. In contrast, no apparent photocurrent was detected in the absence of methylviologen for **4** / Au.

Action spectra of **4** / Au electrode in the presence of methylviologen are shown in Figure 9. There is a reasonably agreement between action spectra of **4** / Au system and electronic absorption spectra of **4** in THF. This indicates that generation of photocurrent is attributed to the excited state of the porphyrin moiety. The slight difference for peak position of Soret and Q bands may results from difference between the environments in the porphyrin on the surface and in solution. Possible mechanism is shown in Figure 10. After excitation of the porphyrin, excited singlet and triplet states of the porphyrin are produced. Intermolecular ET from the excited states to MV<sup>2+</sup> yield the charge-separated state which lead to the generation of the photocurrent.

## 1.4 Conclusion

Porphyrin dimers bearing disulfide group were synthesized.

Porphyrin structures were immobilized on gold surface via S-Au bond.

Porphyrin molecular assemblies were kept unique electronic character of porphyrin structure and redox active.

Photocurrent was observed using porphyrin molecular assembly in the presence of methylviologen.

## 1.5 Synthesis

Synthesis of **1**

p-Acetamidobenzaldehyde (9.8g, 0.06mmol) and p-tolualdehyde (21.6g, 0.18mmol) was dissolved in propionic acid (500ml). The solution was heated to reflux and pyrrole (16.2g, 0.24mmol) was added. Reflux was kept for 30min. and the reaction mixture was cooled to room temperature. The reaction mixture was filtered, and the filtrated purple solid was washed with enough amount of MeOH. Obtained crude porphyrins (2.8g) were separated with flush column chromatography ( $\text{CH}_2\text{Cl}_2$ ). The second band was collected and concentrated under reduced pressure, and the residue was recrystallized from  $\text{CH}_2\text{Cl}_2$  / Hex to give porphyrin 1 as purple crystal (0.48g, 0.67mmol, 1.1%).

1: purple crystal, mp >300 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  = 8.85 (m, 8H), 7.82(dd, 12H, J = 7.8Hz), 7.87 (m, 4H), 2.75 (s, 9H), 2.40 (s, 3H), -2.50 (brs. 2H).

#### Synthesis of 2

Porphyrin 1 (100mg, 0.14mmol) was dissolved in EtOH-1N HCl (40ml : 70ml). The solution was refluxed overnight and poured into  $\text{NaHCO}_3\text{aq}$ . The organic layer was concentrated under reduced pressure, and the residue was purified with flush column chromatography ( $\text{CH}_2\text{Cl}_2$ ). The first band was collected and evaporated and the residue was recrystallized to give 2 as purple crystal (35.3mg, 0.053mmol, 37.9%)

2: purple crystal, mp >300 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  = 8.91 (d, 2H, J = 2.4Hz), 8.84 (d, 6H, J = 1.6Hz), 7.82 (dd, 12H, J = 7.8Hz), 7.53 (dd, 4H, J = 4.6Hz), 2.75 (s, 9H), -2.50 (brs. 2H).

#### Synthesis of 4

3 (81.0mg, 0.186mmol) and 6-chloro-2,4-dimethoxy-1,3,5-triazine (64.0mg, 0.365mmol) were dissolved in dry THF (20ml) which were cooled to under 0°C with ice-salt bath. N-methylmorpholin (40.0ml, 0.365mmol) was added to the solution with dropwise, and stirred for 1hr. Porphyrin 2 (250mg, 0.372mmol) and N-methylmorpholin (40.0ml, 0.365mmol) were added to the reaction mixture, and stirred for 14hr at room temperature. The reaction mixture was poured into 1N HCl. The organic layer was extracted with  $\text{CH}_2\text{Cl}_2$  and neutralized with  $\text{NaHCO}_3\text{aq}$ . The organic layer was concentrated under reduced pressure and the residue was purified by preparative HPLC (GPC). The area of 4 was collected and evaporated. The residue was recrystallized from  $\text{CH}_2\text{Cl}_2$  / hex to give porphyrin 4 as dark red

powder (170mg, 0.098mmol, 52.7%).

**4**: dark red powder, mp >300 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ = 8.83 (s, 8H), 8.81 (s, 8H), 7.3 - 8.2 (m, 32H), 4.25 (brs., 2H), 2.69 (t, 4H), 2.66 (t, 18H), 2.44 (t, 4H), 1.83 (m, 4H), 1.71 (m, 4H), 1.35 (m, 24H), -2.50 (brs., 4H). Calcd. for C<sub>116</sub>H<sub>112</sub>N<sub>10</sub>S<sub>2</sub>O<sub>2</sub> : C, 79.96; H, 6.48; N, 8.04. Anal. Found : C79.65; H, 6.31; N, 7.64.

## Synthesis of **5**

**4** (10.0mg, 5.74μmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20ml). MeOH saturated Zn (OAc)<sub>2</sub> (1ml) was added to the solution. The reaction mixture was stirred for 30 min at room temperature. The solution was purified column chromatography (almina, CH<sub>2</sub>Cl<sub>2</sub>). Pink colored band was collected and evaporated. The residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> / MeOH to give porphyrin **5** as dark red powder (8.5mg, 4.59mmol, 80.0%)

**5**: dark red powder, mp >300 °C.

## 1.6 Refereneces

- 1) M. R. Wasielewski, *Chem. Rev.*, **92**, 435-461 (1992) ; D. Gust and T. A. Moore, "Advanced in Photochemistry, Volume 16, Mimicking Photosynthetic Electron and Energy Transfer," John Wiley & Sons, Inc.
- 2) A. T. Hubbard, *Chem. Rev.*, **88**, 633-656 (1988).
- 3) A. Ulman, "An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly," Academic Press, Inc., New York (1991).
- 4) C. D. Bain, J. Evall, and G. M. Whitesides, *J. Am. Chem. Soc.*, **111**, 7155-7164 (1989).
- 5) M. D. Porter, T. B. Bright, D. L. Allara, and C. E. D. Chidsey, *J. Am. Chem. Soc.*, **109**, 3559-3568 (1987).
- 6) J. J. Hickman, D. Ofer, C. Zou, M. S. Wrighton, P. E. Laibinis, and G. M. Whitesides. *J. Am. Chem. Soc.*, **113**, 1128-1132 (1991).
- 7) C. E. D. Chidsey, C. R. Bertozzi, and A. M. Muijsce, *J. Am. Chem. Soc.*, **112**, 4301-4306 (1990).
- 8) M. Collinson, E. F. Bowden, and M. J. Tarlov, *Langmuir*, **8**, 1247-1250 (1992).
- 9) J. Zak, H. Yuan, M. Ho, L. K. Woo, and M. J. Porter, *Langmuir*, **9**, 2772-2774 (1993).

- 10) A. J. Black, T. T. Wooster, W. E. Geiger, and M. N. Paddon-Row, *J. Am. Chem. Soc.*, **115**, 7924-7925 (1993).
- 11) C. A. Hunter and J. K. M. Sanders. *J. Am. Chem. Soc.*, **112**, 5525-5534 (1990).
- 12) J. P. Collman and S. E. Groh. *J. Am. Chem. Soc.*, **104**, 1391-1405 (1982).
- 13) F. G. Bordwell and W. A. Hewett, *J. Org. Chem.*, **22**, 980-981 (1957).
- 14) T. W. Greene and P. G. M. Wuts, "Protecting Groups in Organic Synthesis Second Edition," John Wiley & Sons, Inc. p.298.
- 15) S. R. Sandler and W. Karo, "Organic Functional Group Preparations I ,Second Edition," Academic Press, Inc., New York (1983), p.598.
- 16) R. G. Little, J. A. Anton, P. A. Loach, and J. A. Ibers, *J. Heterocyclic. Chem.*, **12**, 343 (1975).
- 17) T. W. Greene and P. G. M. Wuts, "Protecting Groups in Organic Synthesis ,Second Edition," John Wiley & Sons, Inc. p.351.
- 18) Z. J. Kaminski, *Synthesis*, 917 (1987).
- 20) J. Huang and J. C. Hemminger, *J. Am. Chem. Soc.*, **115**, 3342-3343 (1993) ; J. E. Hutchison, T. A. Postlethwaite, and R. W. Murray, *Langmuir*, **9**, 3277-3283 (1993) ; S. D. Evans, A. Ulmann, K. E. Goppert-Berarducci, and L. J. Gerenser, *J. Am. Chem. Soc.*, **113**, 5866-5868 (1991).
- 21) E. Laviron, *J. Electroanal. Chem.*, **101**, 19-28 (1979).

# 2

## Synthesis and Self-Assembly of Porphyrin-linked Fullerene on Gold Surface Using S-Au Linkage

### 2.1 Introduction

The relatively small photocurrent was seen in states of the 4 / Au system. This means that intramolecular electron transfer from the excited states of the porphyrin to methylviologen is slower compared with the decay of the excited states of the porphyrin. To generate photocurrent more efficiently. The aim of this study is construction of multistep electron transfer system which mimic photosynthesis. Such multistep electron transfer reactions could produce charge separated states with high quantum yield. To control intermolecular ET, suitable donor and acceptor should be chosen linked together in moderate manner. Porphyrins also employed as a light harvesting donor and fullerene as an acceptor. There are some advantages for usage of fullerenes as an acceptor : i) fullerenes are stable and durable under severe conditions. ii) fullerenes are good electron acceptor. iii) fullerenes accelerate CS and retard back ET. These unique characteristics provide a new opportunity for challenging supra molecular ET relay using porphyrin-linked fullerenes.

Porter et al. reported that methylphenylsulfide makes mixed SAM consisting of Ph-S-Au and Me-S-Au. Since sulfide group is easy to handle compared with thiol and disulfide group, methylthio group was used for formation of SAM on gold surface. As followed above, porphyrin-linked fullerenes containing methylthio group was designed (Fig. 11). Bearing these in mind, such molecules and sequential vectorial ET relay occurs after the excitation of the chromophores. Thus, initial efficient CS within the porphyrin-linked fullerenes followed by intermolecular ET to  $MV^{2+}$ , which eventually produce photocurrent.



## 2.2 Experimental

The synthesis of **9** was carried out as shown in Scheme 2. The pyrrole was converted to dippyromethane **6** by treatment with 3,5-di(*t*-butyl)benzaldehyde in the presence of trifluoroacetic acid. Acid catalyzed condensation of **6** with 4-methylthiobenzaldehyde and monoprotected aromatic dialdehyde (1 : 1 ratio) followed by treatment with  $\text{Zn}(\text{OAc})_2$  in  $\text{CHCl}_3$  gave a mixture of several porphyrins. The desired product was separated by flash column chromatography (Fujisilisia BW300 /  $\text{C}_6\text{H}_6$ ) and hydrolyzed to give **8**. Porphyrin-linked  $\text{C}_{60}$  **9** was obtained by 1,3-dipolar cycloaddition using **8**, *N*-methylglycine, and  $\text{C}_{60}$  in toluene in 94% yield. Reference **11** was obtained by acid catalyzed-coupling of pyrrole, 3,5-di(*t*-butyl)benzaldehyde, and 4-methylthiobenzaldehyde. Reference **13** and **14** were synthesized by 1,3-dipolar cycloaddition of the corresponding azomethine ylide to  $\text{C}_{60}$  as described for **9**. Structures of all new compounds were confirmed by spectroscopic analysis. An gold electrode with Au (111) surface was purchased from SHIBAO. This electrode was prepared by sequential vacuum deposition of Cr layer (50Å) and gold layer (2000Å) on Si (100) wafer (SUMITOMO SITX CORP) (Fig. 3). The porphyrin molecules were deposited on the gold surface by soaking the electrode in 1mM  $\text{CH}_2\text{Cl}_2$  solution of **9-13** for 4 days to equilibrate adsorption. These samples of these molecules on the surface were washed well with enough amount of  $\text{CH}_2\text{Cl}_2$  and dried with a stream of  $\text{N}_2$ . Electrochemical measurement was performed on Bioanalytical Systems, Inc. CV-50W and Huseo Electro Chemical System, Inc. HECS 315B, HECS 321B, and HECS 311B. Monochromator system for action spectra measurement was JOBIN YVON, Inc. H-19UV and MIC7. Recorder for action spectra measurement was YOKOGAWA 3057. Xe lamp light source for photocurrent measurement was SUMITA OPTICAL GLASS, INC. LS-140UV and LX-300UV. Electrochemical cell for all measurement was shown in Fig. 5. X-ray photoelectron spectroscopy was performed on VG SCIENTIFIC, INC.  $\mu\text{Lab}$  mark III with MgK $\alpha$  X-ray (1253.6 eV, 8kV, 16mA). Molecular mechanics calculation was performed on CAChe.

## 2.3 Results and Discussion

### Properties of molecules

Electronic absorption spectra, Steady-state fluorescence spectra, and Redox potentials

Electronic absorption spectrum of **9** in THF was almost a linear combination of those of **11** and **13**, indicating no appreciable interaction between the two chromophores in the ground state. Similar tendency was observed for **10**, **12**, and **13**. All the absorption spectra was shown in Fig. 12.

Fluorescence spectra (Fig. 13) of **9** and **10** were strongly quenched as compared with those of **11** and **12** (<1% in THF), respectively, showing the rapid quenching of the excited singlet state of the porphyrin by the C<sub>60</sub>.

Redox potentials of **9-13** were measured with cyclic voltammetry in CH<sub>2</sub>Cl<sub>2</sub>. Redox potentials of **9** (1.24, 0.90, -0.67, -1.06, -1.26 V vs. Ag / AgCl) in CH<sub>2</sub>Cl<sub>2</sub> using 0.1 mol dm<sup>-3</sup> Bu<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte can be explained by the sum of **11** (1.20, 0.87, -1.25 V) and **13** (-0.65, -1.04V). Redox potentials of **10** (0.92, 0.67, -0.66, -1.05, -1.43 V) can also be reproduced by the sum of **12** (1.05, 0.71, -1.42 V) and **13**. These results also indicate that there is no significant interaction between the two chromophores in the ground state.

#### Fluorescence lifetime measurement and time-resolved transient absorption spectroscopy

The fluorescence lifetimes of **9-12** were measured by a picosecond time-resolved single-photon counting technique. These molecules in THF were excited at 400nm and monitored at 650-720nm. Fluorescence lifetimes of **9** and **10** in THF are beyond the time resolution (<40ps) of instrumentation, which are consistent with the fluorescence quenching experiment. Photophysical properties of **9** and **10** in THF were investigated by picosecond time-resolved transient absorption spectroscopy. After excitation of **9** and **10** with 590nm picosecond pulse transient species appeared. Within the time-resolution (<20ps) of the instrument. Broad band at around 650nm and 900nm were seen for **9** and **10**, very broad structureless bands (>500nm) were also observed for **9** after the excitation. Concomitant decay of 650nm and 900nm bands in **10** shows that 650nm band is ascribed to the zinc porphyrin cation and 920nm band is to C<sub>60</sub><sup>•-</sup>. Transient species in **9** may be intramolecular exciplex with less CT character. These spectra were shown in Fig. 14.

#### Properties of molecular assemblies

##### X-ray photoelectron spectroscopy

Structures of SAM in **9** / Au and **10** / Au were investigated by XPS. The results were showed in Figure 15. The values due to S(2p) region are in good agreement with the previously reported values of thiolate bound to gold. Furthermore, in the case of **9** / Au, the peaks of S(2p) region for **9** / Au also shows the existence of sulfone, but these peaks disappeared gradually. These results indicate that these molecules are adsorbed on Au through both S-Au and SO<sub>3</sub>-Au linkages.

#### Mass spectroscopy with time of flight method

##### Ga<sup>+</sup> ionization TOF mass

Fig. 16 show Ga<sup>+</sup> ionization TOF mass spectra of **9** / Au. These fragment peaks indicate the existence of porphyrin-linked fullerene structures on gold surface. However, the evident peaks of porphyrin-linked fullerene molecular assembly on gold surface via S-Au bond, the peaks indicate the existence of much weaker SO<sub>3</sub>-Au linkages as biproduct were detected. It may S-Au linkage is too strong to cleave by Ga<sup>+</sup> ionization.

##### Laser ionization TOF mass

Fig. 17 show Laser ionization TOF mass spectra of **9** / Au and **9**. These fragment peaks indicate the existence of porphyrin-linked fullerene structures on gold surface. However, the mother peak was not detected, only the peaks of lacing fullerene moiety were detected.

#### Reflective absorption spectroscopy

Fig. 18 show the results of RAS measurement of **11** / Au. The peak around 3060cm<sup>-1</sup> was assigned to aromatic C-H vibration, and the peaks near 2970, 2905, 2850cm<sup>-1</sup> were assigned to aliphatic C-H vibration. These results were good agreement with reported values.

#### Electrochemical measurement

Fig. 19 show cyclic voltamograms of **9** / Au and **11** / Au. In both the cases irreversible oxidative peaks due to the porphyrin moiety were observed. On the other hand no apperant peaks due to the C<sub>60</sub> moiety were detected for **9** / Au because of extensive cleavage of S-Au bond. Numbers of adsorbed molecules in **9** / Au and **11** / Au were estimated to be 1.6 x 10<sup>-11</sup> mol / cm<sup>2</sup> and 0.6 x 10<sup>-11</sup> mol / cm<sup>2</sup>. These values are much

smaller compared with alkanethiol / Au systems.

### Ellipsometry

The results of ellipsometry measurements showed the thickness of **9** / Au was 13.2 Å.

This value was obtained by fitting of the results of ellipsometric observation.

### Molecular mechanics calculation

Molecular mechanics calculations using the CAChe program yielded the structures shown in Figure 20 as the lowest-energy conformation of porphyrin-linked fullerene **9** with Au surface. S-Au linkage was set to vertical to Au(111) surface minimized and linked to Au surface. Structure of **9** was obtained from suitable conformational search and sequential minimization constraining the structure of the porphyrin moiety to hold the planarity of the porphyrin ring observed by X-ray crystallography. During all procedures the usual CAChe parameters were retained to calculate the optimized structure for **9**.

The results of calculation **9** / Au shows that the height of the molecules is 17 Å, and one molecule occupies 310.6 Å in area. The height is in good agreement with that obtained by ellipsometry. The area per a molecule is roughly consistent with that estimated by the cyclic voltammetry.

### Photocurrent measurement

Photoelectrochemical measurements were carried out using Pyrex cell consisting of modified Au electrode, Ag / AgCl as a reference electrode, and platinum electrode as a counter electrode through 0.1M Na<sub>2</sub>SO<sub>4</sub> aqueous solution. The results of photocurrent measurements were shown in Figure 21 At the negative potential around -200mV vs. Ag / AgCl, the large cathodic photocurrent was clearly seen for **9** / Au in the presence of methylviologen compared with that under no light. In contrast, no apparent photocurrent was detected for **11** / Au in the absence of methylviologen. On the other hand, no significant photocurrent was observed for **10** / Au and **12** / Au in the presence of MV<sup>2+</sup>. Action spectra of **9** / Au system in the presence of methylviologen are shown in Figure 22 which corresponds well to electronic absorption spectrum of **9** in THF, indicating that generation of the photocurrent is mainly due to the excited singlet state of the porphyrin is strongly quenched by the attached C<sub>60</sub> and followed by formation of

the exciplex with a long lifetime, direct intermolecular ET from the exciplex to  $MV^{2+}$  may lead to subsequent charge-separated state ( $H_2P^+-C_{60}-MV^+$ ). Magnitude of the photocurrent for **9** / Au system increases of  $MV^{2+}$ , showing that rate-determining step is intermolecular ET from the exciplex to  $MV^{2+}$ . This is supported by the fact that the photocurrent is much smaller compared with that in the presence of benzylviologen. No apparent photocurrent was observed in the case of **10** / Au. Possible explanation is that the rate for intermolecular ET from the  $C_{60}^-$  in charge-separated state ( $ZnP^+-C_{60}^-$ ) because  $ZnP^+-C_{60}^-+MV^{2+}$  and  $ZnP^+-C_{60}^-+MV^+$  are similar in energy. The fact that  $BV^{2+}$  instead of  $MV^{2+}$  increases the photocurrent is consistent with this reaction mechanism. Possible mechanism is shown in Figure 23.

## 2.4 Conclusion

Porphyrin-linked fullerenes bearing methylthio group were synthesized.

Porphyrin-linked fullerenes structure were immobilized on gold surface via S-Au bond.

A large photocurrent was observed using freebase porphyrin-linked fullerene assembly in the presence of methylviologen.

A large photocurrent using freebase porphyrin-linked fullerene assembly was produced via singlet excited state of porphyrin moiety.

## 2.5 Synthesis

Synthesis of methyl-4-(5,5-dimethyl-1,3-dioxan-2-yl)-benzoate.

To a solution of 4-Methoxycarbonyl-benzaldehyde (32.8g, 0.20mol) and 2,2-dimethyl-1,3-propanediol (20.8g, 0.20mol) in benzene (500ml) was added p-TsOH (3.80g, 0.02mol). The mixture was refluxed for 15h with dehydration by dean-stark. After cooling, the solution was neutralized with  $NaHCO_3$  aq. The organic layer was separated and dried over  $Na_2SO_4$ . The organic solvent was removed under reduced pressure and the residue was dissolved with  $CHCl_3$  (250ml). The  $CHCl_3$  layer was washed with 15%  $Na_2S_2O_4$  aq and water. The organic layer was evaporated to give methyl-4-(5,5-dimethyl-1,3-dioxan-2-yl)-benzoate (48.31g,

0.193mol, 97% yield).

methyl-4-(5,5-dimethyl-1,3-dioxan-2-yl)-benzoate: White powder.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  = 8.05 (d, 2H,  $J$  = 8.1Hz), 7.58 (d, 2H,  $J$  = 8.1Hz), 5.43 (s, 1H), 3.91 (s, 3H), 3.79 (d, 2H,  $J$  = 10.8Hz), 3.66 (d, 2H,  $J$  = 10.8Hz), 1.29 (s, 3H).

#### Synthesis of 4-(5,5-dimethyl-1,3-dioxan-2-yl) benzylalcohol.

To a solution of methyl-4-(5,5-dimethyl-1,3-dioxan-2-yl)-benzoate (48.3g, 0.19mol) in THF (400ml) was added  $\text{LiAlH}_4$  (12.07g, 0.32mol) at  $0^\circ\text{C}$ . The mixture was stirred for 12h. The reaction was quenched with EtOAc and  $\text{H}_2\text{O}$  at  $0^\circ\text{C}$ , and 1M  $\text{HCl}$  aq, it was extracted with EtOAc. The organic layer was washed with water, and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure to give 4-(5,5-dimethyl-1,3-dioxan-2-yl) benzylalcohol as oil (41.7g, 0.188mol, 97% yield).

4-(5,5-dimethyl-1,3-dioxan-2-yl) benzylalcohol: Colorless oil.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  = 7.50 (d, 2H,  $J$  = 8.1Hz), 7.36 (d, 2H,  $J$  = 8.1Hz), 5.39 (s, 1H), 4.67 (s, 2H), 3.77 (d, 2H,  $J$  = 10.8Hz), 3.65 (d, 2H,  $J$  = 10.8Hz), 2.50 (br.s, 1H), 1.29 (s, 3H), 0.80 (s, 3H).

#### Synthesis of 4-(5,5-dimethyl-1,3-dioxan-2-yl) benzaldehyde.

To a solution of 4-(5,5-dimethyl-1,3-dioxan-2-yl) benzylalcohol (41.7g, 0.188mol) in  $\text{CH}_2\text{Cl}_2$  (200ml) was added PCC (60.6g, 0.282mol) dropwise, and  $\text{CH}_3\text{CO}_2\text{Na}$  (6.17g, 0.08mol). The mixture was stirred for 3h at R.T. Ether (200ml) was added to the reaction mixture. After filtration, the filtrate was purified through florisil. The solution was evaporated, and the residue was recrystallized from hexane / MeOH to give 4-(5,5-dimethyl-1,3-dioxan-2-yl) benzaldehyde. (20.42g, 0.09mol, 48% yield).

4-(5,5-dimethyl-1,3-dioxan-2-yl) benzaldehyde.: white crystal.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  = 10.0 (s, 1H), 7.89 (d, 2H,  $J$  = 8.1Hz), 7.68 (d, 2H,  $J$  = 8.1Hz), 5.45 (s, 1H), 3.80 (d, 2H,  $J$  = 10.8Hz), 3.67 (d, 2H,  $J$  = 10.8Hz), 1.29 (s, 3H), 0.82 (s, 3H).

#### Synthesis of 6

3,5-di-tert-butyl-benzaldehyde (21.8g, 0.1mol) was dissolved in distilled pyrrole (280ml, 4.0mol). The mixture was bubbled with  $\text{N}_2$  for 15min and  $\text{CF}_3\text{COOH}$  (0.08ml, 1mmol) was

added and stirred for 15min. To the mixture was poured  $\text{CHCl}_3$  (1000ml) and washed with 0.1M  $\text{NaOH}$  aq,  $\text{H}_2\text{O}$ . The organic layer was dried over  $\text{Na}_2\text{SO}_4$  and the solvent was removed under reduced pressure. The residue was purified flush column chromatography ( $\text{CHCl}_3$ ). The second band was collected and evaporated to give **6** (18.41g, 55.1mmol, 55% yield).

**6**: pink crystal, mp  $>300^\circ\text{C}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  = 7.91 (br.s, 2H), 7.31 (t, 1H,  $J$  = 1.7Hz), 7.06 (d, 2H,  $J$  = 1.7Hz), 6.69 (q, 2H,  $J$  = 1.7Hz), 6.15 (q, 2H,  $J$  = 3.0Hz), 5.93, (br.s, 2H), 5.45 (s, 1H), 1.28 (s, 18H).

### Synthesis of **7**

**6** (18.41g, 55.1mmol), **3** (6.06g, 25.0mmol), and 4-methylthio-benzaldehyde (3.64ml, 25.0mmol) were dissolved in  $\text{CH}_3\text{CN}$  (700ml). The mixture was stirred overnight. To the solution was added Chloranil (3g) stirred for additional 5h. The mixture was washed with  $\text{NaHCO}_3$  aq and  $\text{NaCl}$  aq. The organic layer was separated and dried over  $\text{Na}_2\text{SO}_4$ . After filtration, to the mixture a saturated  $\text{Zn}(\text{OAc})_2$  MeOH solution (50ml) was added. The mixture was refluxed for 3h. The solvent was removed under reduced pressure, and the residue was purified with flush column chromatography (benzene). The second band was collected and evaporated to give **7** (531.5mg, 12.5mmol, 2% yield).

**7**: purple powder, mp  $>300^\circ\text{C}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  = 9.00 - 8.90 (m, 8H), 8.25 (d, 2H,  $J$  = 7.9Hz), 8.13 (d, 2H,  $J$  = 7.9Hz), 8.09 (d, 4H,  $J$  = 1.7Hz), 7.90 (d, 2H,  $J$  = 7.9Hz), 7.80 (t, 2H,  $J$  = 1.7Hz), 7.58 (d, 2H,  $J$  = 7.9Hz), 5.75 (s, 1H), 3.96 (d, 2H,  $J$  = 10.9Hz), 3.85 (d, 2H, 10.9Hz), 2.69 (s, 3H), 1.52 (s, 36H), 1.48 (s, 3H), 0.91 (s, 3H). MS (FAB) 1065 ( $\text{M}+1$ )<sup>+</sup>. Calcd. for  $\text{C}_{67}\text{H}_{72}\text{N}_4\text{O}_2\text{SZn}$  : C, 75.72; H, 6.83; N, 5.27; O, 3.01; S, 3.02; Zn, 6.15. Anal. Found : C, 76.00; H, 6.61; N, 5.15

### Synthesis of **8**

**7** (107.0mg, 0.10mmol),  $\text{CF}_3\text{COOH}$  (5ml),  $\text{CH}_3\text{COOH}$  (10ml) and 5%  $\text{H}_2\text{SO}_4$  (2.5ml) were mixed in the flask. The reaction mixture was heated to  $100^\circ\text{C}$  and stirred for 2h. The solution was diluted with water and extracted with  $\text{CHCl}_3$ . The organic layer was washed with  $\text{NaHCO}_3$  aq and dried over  $\text{Na}_2\text{SO}_4$ . After filtration, the solvent was evaporated and the residue was purified with flush column chromatography (benzene). The red band was collected

and triturated with MeOH to give **8** (71.3mg, 0.08mmol, 80% yield).

**8**: Purple powder, mp >300 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ = 10.4 (s, 1H), 8.85 - 8.30 (m, 8H), 8.42 (d, 2H, J = 8.2Hz), 8.28 (d, 2H, J = 8.2Hz), 8.15 (d, 2H, J = 8.2Hz), 8.08 (d, 4H, J = 1.7Hz), 7.81 (t, 2H, J = 1.7Hz), 7.63 (d, 2H, J = 8.2Hz), 2.75 (s, 3H), 1.53 (s, 36H), -2.73 (br.s, 2H). MS (FAB) 913 (M+1)<sup>+</sup>. Calcd. for C<sub>62</sub>H<sub>64</sub>N<sub>4</sub>O<sub>8</sub>S : C, 81.54; H, 7.06; N, 6.13; O, 1.75; S, 3.51. Anal. Found : C, 81.32; H, 6.91; N, 6.01

### Synthesis of **9**

**8** (60.0mg, 0.066mmol), C<sub>60</sub> (94.0mg, 0.13mmol) and N-methylglycine (117mg, 1.3mmol) were dissolved in toluene (28ml). The mixture was refluxed for 6h. The solvent was removed under reduced pressure, and the residue was purified flush column chromatography (hexane / benzene = 1 / 1). First band was collected and evaporated, and the residue was recrystallized from benzene / MeOH to give **9** as purple powder (103.0mg, 0.062mmol, 94% yield).

**9**: purple powder, mp >300 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ = 9.00 - 8.70 (m, 8H), 8.20 - 7.80 (br.m, 10H), 7.78 (br.s, 2H), 7.60 (d, 2H, J = 8.6Hz), 4.45 (d, 1H, J = 8.6Hz), 3.92 (s, 1H), 3.36 (d, 1H, J = 8.6Hz), 2.86 (s, 3H), 2.71 (s, 3H), 1.53 (s, 36H), -2.70 (br.s, 2H). <sup>13</sup>C-NMR (67.5 MHz, CDCl<sub>3</sub>) δ 31.2, 31.6, 32.0, 32.4, 35.1, 67.7, 75.8, 76.2, 78.0, 78.6, 119.3, 119.5, 120.5, 121.5, 121.8, 122.2, 123.3, 125.0, 125.6, 129.4, 130.4, 131.6, 133.5, 134.0, 135.0, 135.9, 136.2, 138.1, 138.2, 138.6, 138.7, 139.1, 139.5, 140.5, 140.6, 140.7, 141.0, 141.2, 141.4, 141.5, 141.7, 141.8, 142.4, 142.6, 142.9, 143.1, 143.3, 143.5, 143.7, 143.8, 143.9, 144.1, 144.2, 144.3, 144.8, 145.0, 145.1, 145.2, 145.3, 146.4, 148.8, 151.0, 152.1, 154.8 ppm. MS (FAB) 1662 (M+1)<sup>+</sup>. UV-Vis (THF) λ max 420, 515, 552, 591, 649 nm. Calcd. for C<sub>124</sub>H<sub>69</sub>N<sub>5</sub>S : C, 89.67; H, 4.19; N, 4.22; S, 1.93. Anal. Found : C, 89.91; H, 4.30; N, 3.99

### Synthesis of **10**

**9** (13.0mg, 7.82μmol) was dissolved in CHCl<sub>3</sub> (20ml). Zn(OAc)<sub>2</sub> saturated MeOH solution (2ml) was added to the porphyrin solution. The solution was refluxed for 30min. The reaction mixture was poured into water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The residue was purified with flush column chromatography (hexane / benzene = 1 /



1). The red band was collected and evaporated and the residue was recrystallized from benzen / MeOH to give **10** as brown powder (12.3mg, 7.13umol, 91% yield).

**10**: brown powder, mp >300 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ = 9.00 - 8.60 (br.m, 8H), 8.20 - 7.80 (br.m, 12H), 7.89 (br.s, 2H), 4.21 (d, 1H, J = 7.9Hz), 3.39 (s, 1H), 3.00 (br.s, 1H), 2.78 (s, 3H), 2.46 (s, 3H), 1.51 (s, 36H). MS (FAB) 1725 (M+1)<sup>+</sup>. Calcd. for C<sub>12</sub>H<sub>69</sub>N<sub>5</sub>SZn : C, 86.37; H, 4.00; N, 4.03; S, 1.84; Zn, 3.76. Anal. Found : C, 86.71; H, 4.32; N, 3.84

### Synthesis of **11**

3,5-di-tert-bu-benzaldehyde (6.13g, 28.1mmol), 4-methylthiobenzaldehyde (1.42g, 9.37mmol, 1.25ml), and distilled pyrrole (2.51g, 3.75mmol, 2.6ml) were dissolved in dry CHCl<sub>3</sub> (900ml). The mixture was degassed with N<sub>2</sub>. Then, BF<sub>3</sub>(OEt)<sub>2</sub> (3.2ml) was added to the solution and stirred for 2hr with N<sub>2</sub> atmosphere. Chloranil (6.92g) was added to the reaction mixture and stirred for over night. The solvent was removed under reduced pressure, and the residue was purified two times with column chromatography (BW300, CHCl<sub>3</sub>, benzen / hexane = 1 / 1). The second band was collected and evaporated. The residue was recrystallized from benzen / CH<sub>3</sub>CN to give **11** as dark red powder (0.12g, 0.12mmol, 13% yield).

**11**: reddish powder, mp >300 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ = 8.91 - 8.86 (m, 8H), 8.15 (d, 2H, J = 8.3Hz), 8.10 (d, 4H, J = 2.0Hz), 8.09 (d, 2H, J = 1.6Hz), 7.80 (t, 1H, J = 1.6Hz), 7.79 (t, 2H, J = 2.0Hz), 7.61 (d, 2H, J = 8.3Hz), 2.72 (s, 3H), 1.53 (s, 54H), -2.69 (br. s. 2H). MS (FAB) 998 (M+1)<sup>+</sup>. Calcd. for C<sub>69</sub>H<sub>80</sub>N<sub>4</sub>S : C, 83.09; H, 8.08; N, 5.62; S, 3.21. Anal. Found : C, 83.21; H, 8.22; N, 5.35

### Synthesis of **12**

To a solution of **11** (0.11g, 0.12mmol) in CHCl<sub>3</sub> (100ml) was added a saturated Zn(OAc)<sub>2</sub> in MeOH solution (10ml). The mixture was refluxed for 10min. After cooling, the organic layer was washed with water, and the CHCl<sub>3</sub> layer was dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the residue was purified with column chromatography (BW300, benzen / hexane = 1 / 1). Colored band was evaporated and recrystallized from benzen / MeOH to give **12** as pink powder (60mg, 0.057mmol, 47% yield)

**12:** pink powder, mp >300 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ = 9.00 - 8.96 (m, 8H), 8.15 (d, 2H, J = 8.2Hz), 8.09 (d, 4H, J = 2.0Hz), 8.09 (d, 2H, 2.3Hz), 7.79 (t, 2H, 2.0Hz), 7.78 (t, 1H, 2.3Hz), 7.63 (d, 2H, J = 8.2Hz), 2.73 (s, 3H), 1.52 (s, 54H). MS (FAB) 1061 (M+1)<sup>+</sup>. Calcd. for C<sub>69</sub>H<sub>78</sub>N<sub>4</sub>SZn :C, 78.12; H, 7.41; N, 5.28; S, 3.02; Zn, 6.16. Anal. Found : C, 77.93; H, 7.15; N, 5.38

## 2.6 Reference

- 1) M. R. Wasielewski, *Chem. Rev.*, **92**, 435 (1992).
- 2) "Molecular Electronic Devices," ed by F. L. Carter, R. E. Siatkowski, and H. Wohltjen, Norte-Holland, Amsterdam (1988).
- 3) P. Seta, E. Bienvenue, A. L. Moore, P. Mathis, R. V. Bensasson, P. A. Liddell, P. J. Pessiki, A. Joy, T. A. Moore, and D. Gust, *Nature*, **316**, 653 (1985).
- 4) Y. Sakata, H. Tatemitsu, E. Bienvenue, and P. Seta, *Chem. Lett.*, **1988**, 1625.
- 5) M. Fujihira, M. Nishiyama, and H. Yamada, *Thin Solid Films*, **132**, 77 (1986).
- 6) J. J. Hickman, D. Ofer, C. Zou, M. S. Wrighton, P. E. Laibinis, and G. M. Whitesides, *J. Am. Chem. Soc.*, **113**, 1128 (1991).
- 7) A. J. Black, T. T. Wooster, W. E. Geigen, and M. W. Paddon-Row, *J. Am. Chem. Soc.*, **115**, 7924 (1993).
- 8) C.-J. Zhong and M. D. Porter, *J. Am. Chem. Soc.*, **116**, 11616 (1994).
- 9) T. Akiyama, H. Imahori, and Y. Sakata, *Chem. Lett.*, **1994**, 1447.
- 10) A. Ulman, "An Introduction to Ultrathin Organic Films From Langmuir-Blodgett to Self-Assembly," Academic Press, San Diego (1991).
- 11) A. T. Hubbard, *Chem. Rev.*, **88**, 633 (1988).
- 12) T. Kondo, S. Nomura, and K. Uosaki, 64th National Meeting of the Chemical Society of Japan, Tokyo, March 1994, Abstr. No. 1L526.
- 13) S. Yamada, H. Kohroggi, and T. Matsuo, *Chem. Lett.*, **1995**, 639.
- 14) H. Imahori, K. Hagiwara, T. Akiyama, S. Taniguchi, T. Okada, and Y. Sakata, *Chem. Lett.*, **1995**, 265.
- 15) H. Imahori and Y. Sakata, *Chem. Lett.*, **1996**, 199.
- 16) C.-H. Lee and J. S. Lindsey, *Tetrahedron*, **50**, 11427 (1994).
- 17) T. Nagata, *Bull. Chem. Soc. Jpn.*, **64**, 3005 (1991).
- 18) M. Maggini, G. Scorrano, and M. Prato, *J. Am. Chem. Soc.*, **115**, 9798 (1993).

# Figures, Tables, and Schemes

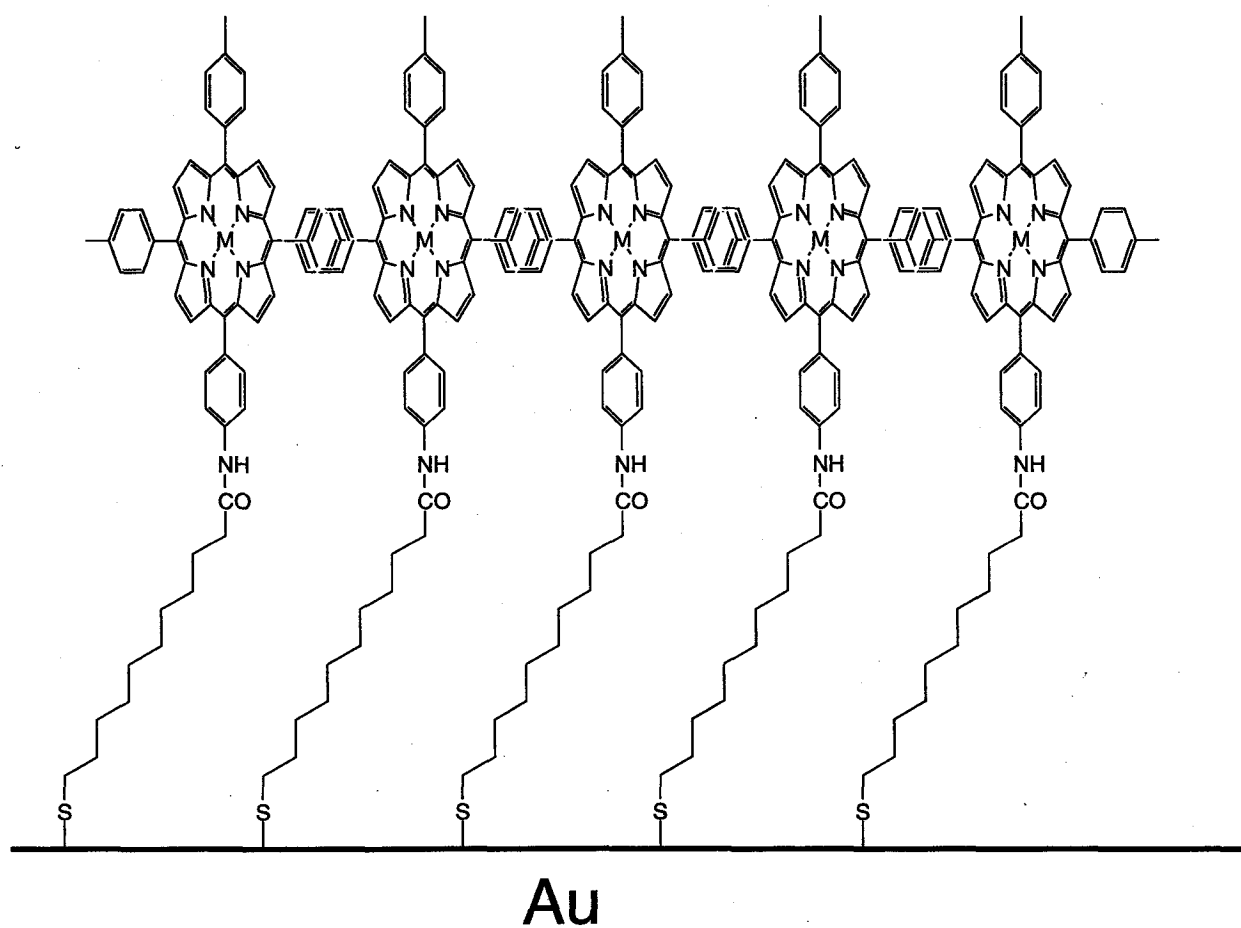


Figure 1 Porphyrin Molecular Assembly

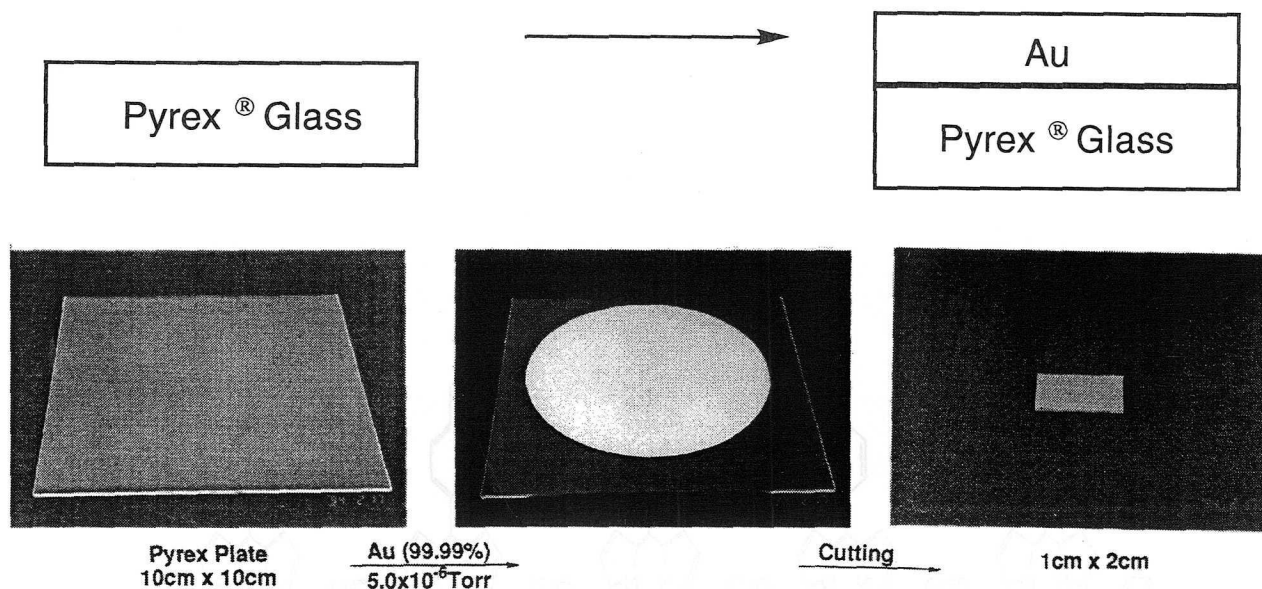
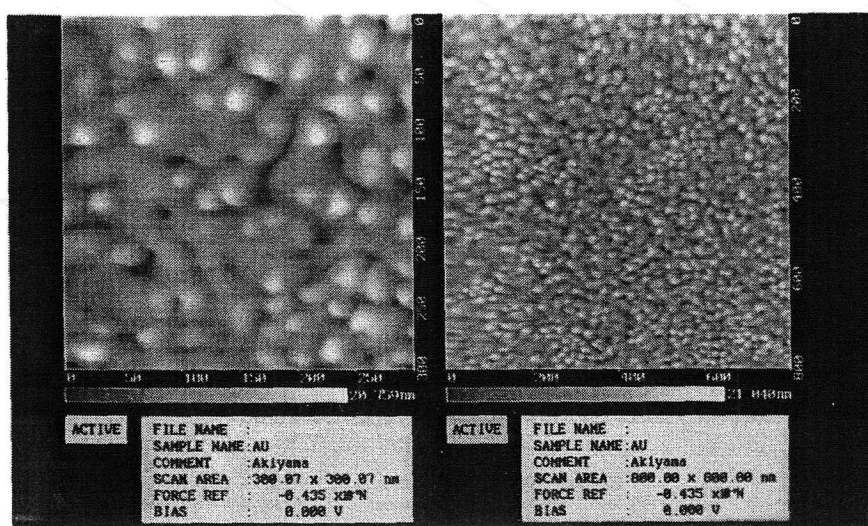


Figure 2 Preparation of Au / Pyrex Electrode

### Atomic Force Microscopy



Surface Roughness  
Maximum = 200Å  
RMS = 27Å

Figure 2-2 AFM Image of Au / Pyrex

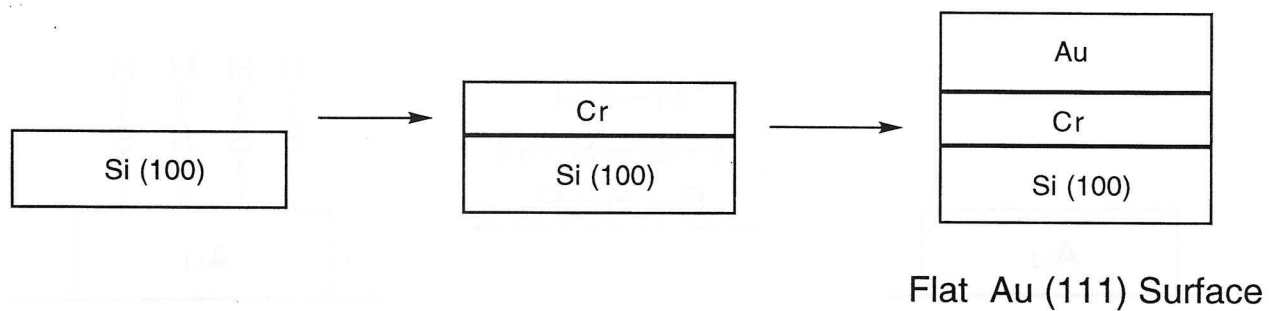


Figure 3 Prepration of Au / Cr / Si (100) Electrode

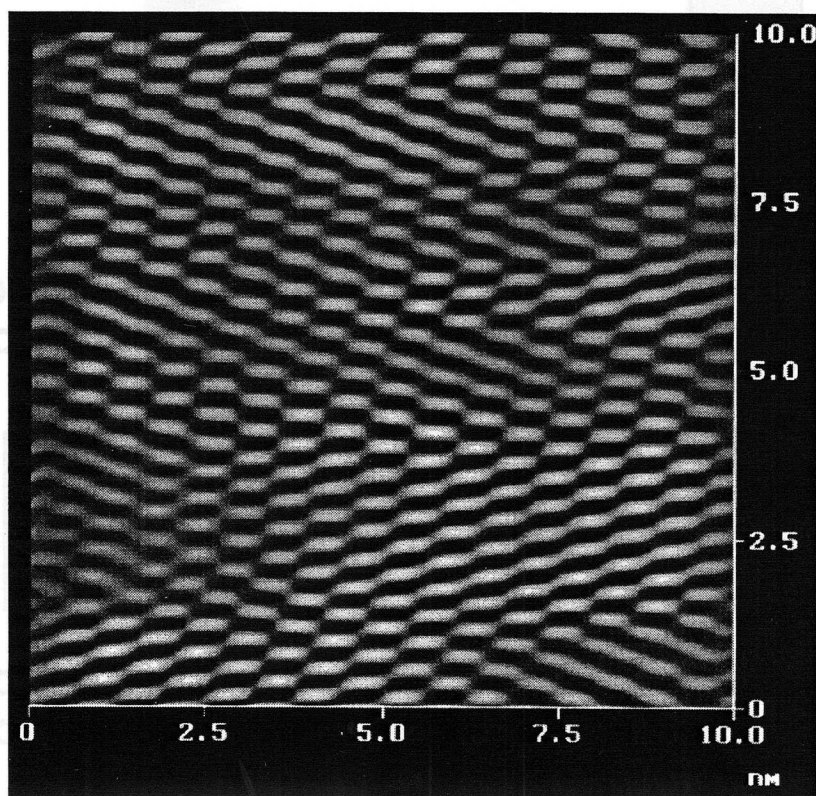


Figure 3-2 AFM Image of Au / Cr / Si (100)

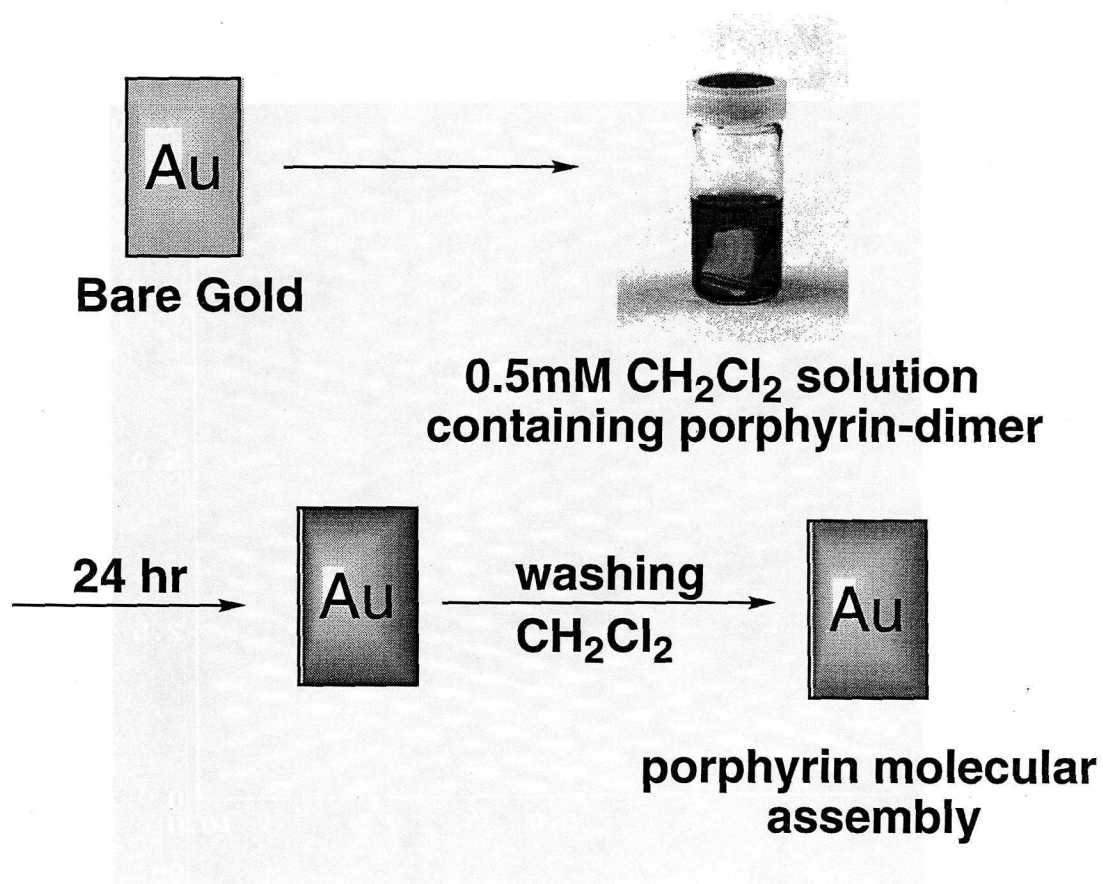
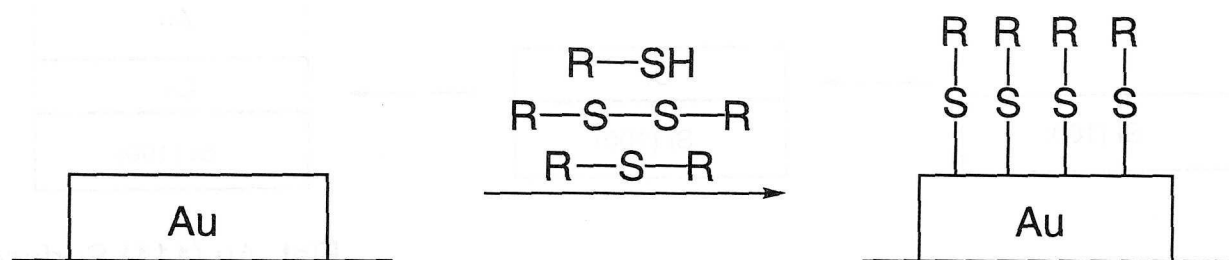


Figure 4 Formation of Self-Assembled Monolayer

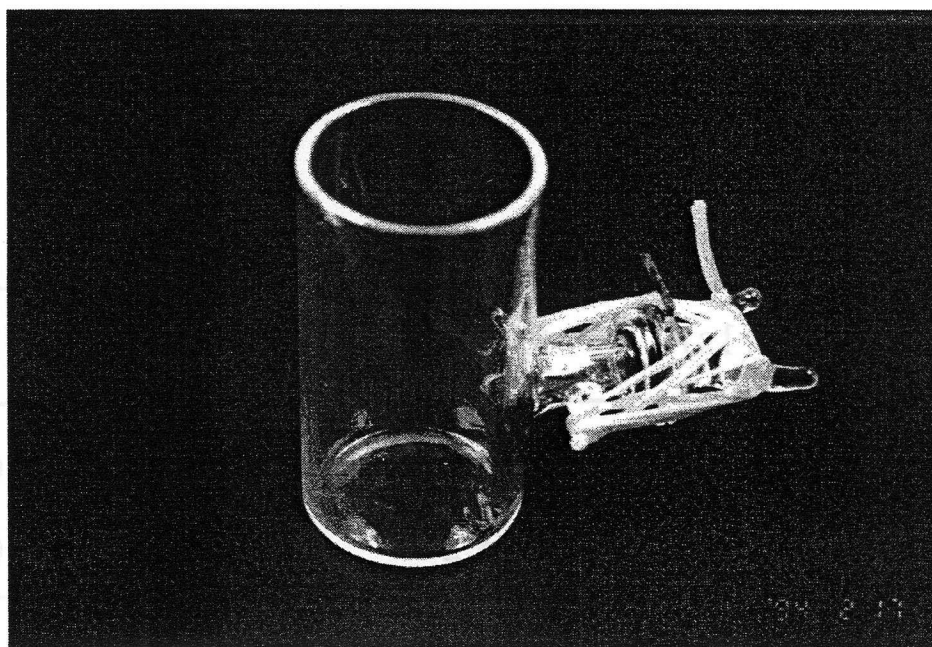
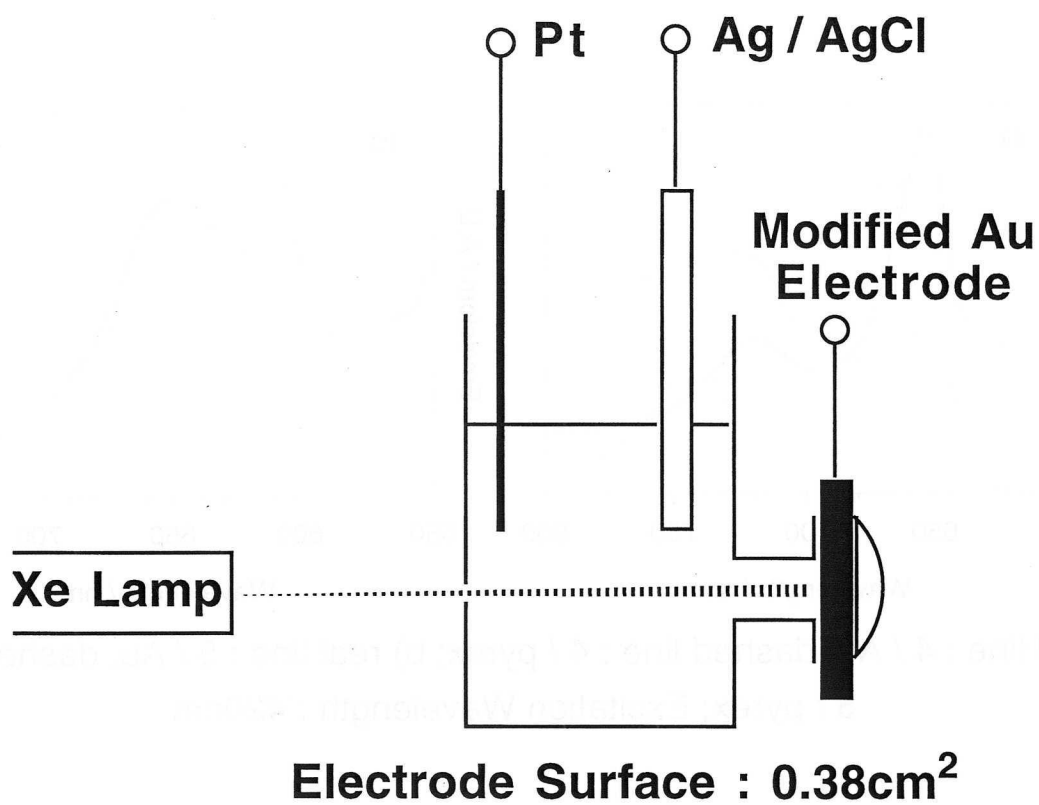
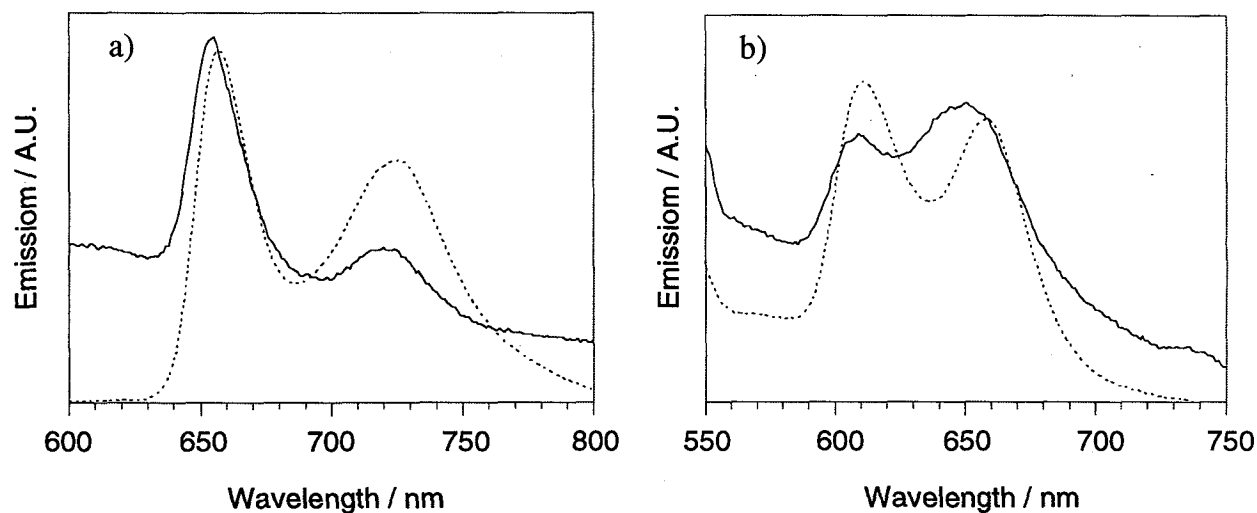


Figure 5 Photoelectrochemical Measurement Cell



a) real line : **4** / Au, dashed line : **4** / pyrex; b) real line : **5** / Au, dashed line : **5** / pyrex; Excitation Wavelength : 420nm

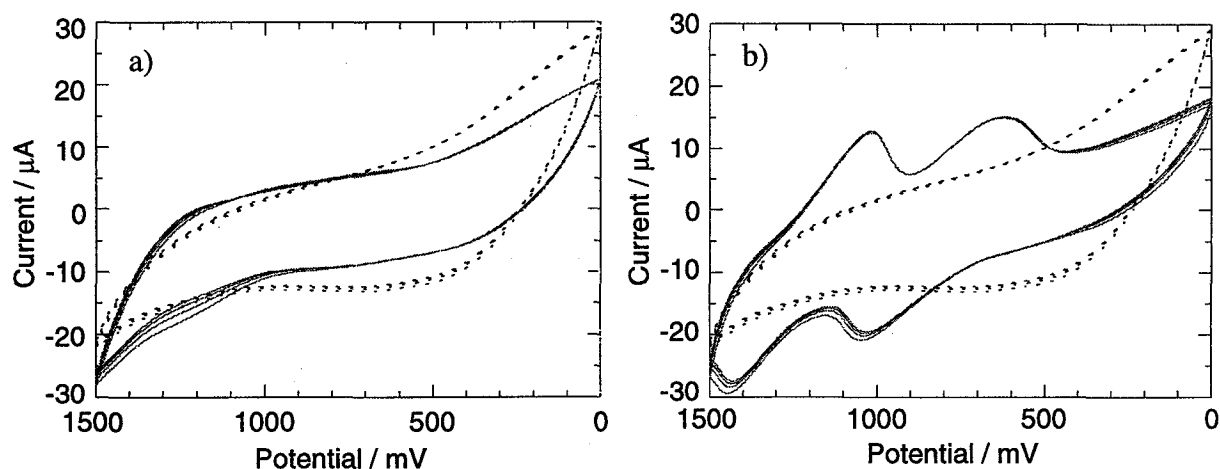
Figure 6 Fluorescence Emission Spectra

|               | C (1s) | O (1s) | N (1s) | S (2p <sup>3/2</sup> ) |
|---------------|--------|--------|--------|------------------------|
| <b>4</b> / Au | 285.0  | 533.0  | 400.0  | 162.1                  |
| <b>5</b> / Au | 285.6  | 533.2  | 399.7  | 162.2                  |

Binding Energy / eV

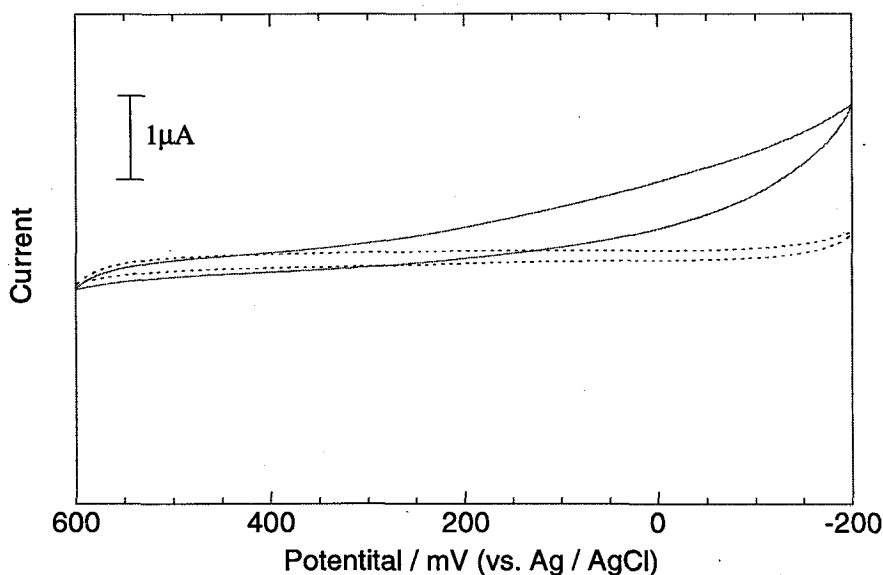
Table 1 Photoelectron Binding Energy





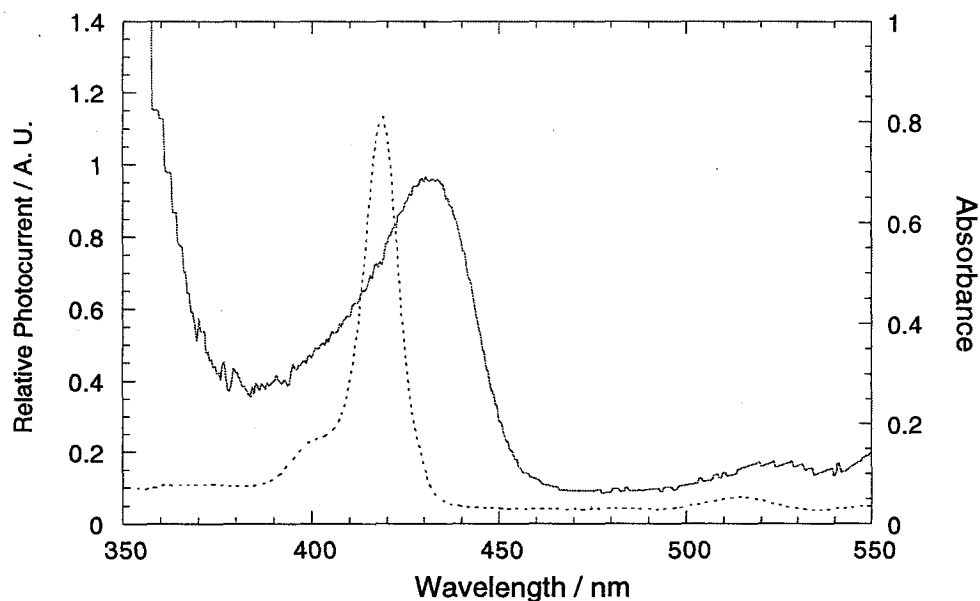
a) real line : **4** / Au, dashed line : bare Au; b) real line : **5** / Au, dashed line : bare Au; Electrolyte : 0.1M n-Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>, reference electrode : Ag / AgCl, counter electrode : Pt wire, scan rate : 500mV / sec

Figure 7 Cyclic Voltammetry



Working Electrode : Modified Au Electrode, Reference Electrode : Ag / AgCl, Counter Electrode : Pt, Supporting Electrolyte: 0.1M Na<sub>2</sub>SO<sub>4</sub>aq, Electron Carrier: 5mM Methylviologen, Light : 150W Xe Lamp, Scan Rate : 500mV / sec, real line : light, dashed line : dark

Figure 8 Photocurrent of **4** / Au



Working Electrode : Modified Au Electrode, Reference Electrode : Ag / AgCl, Counter Electrode : Pt, Supporting Electrolyte: 0.1M Na<sub>2</sub>SO<sub>4</sub>aq, Electron Carrier: 5mM Methylviologen, Light : 300W Xe Lamp, Observed Potential : 0mV, real line : photocurrent of 4 / Au, dashed line : electronic absorption spectrum of 4 in THF

Figure 9 Action Spectrum of 4 / Au

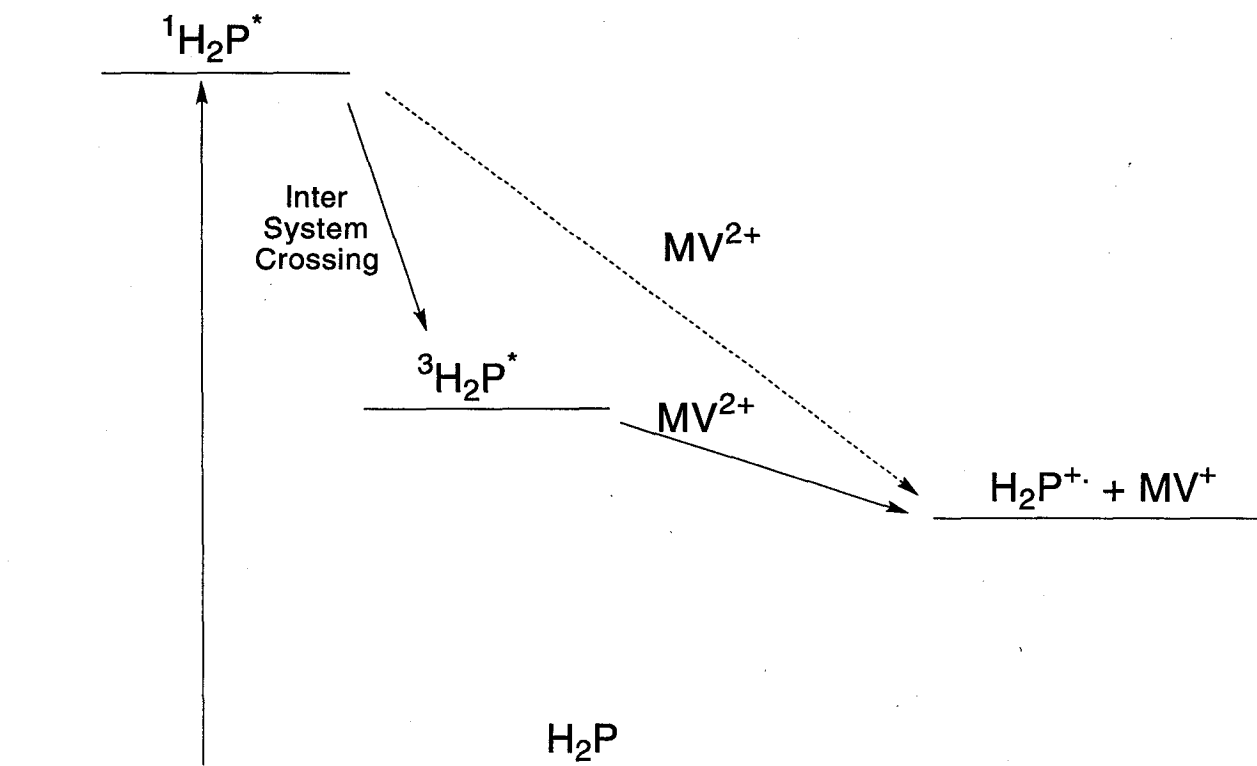
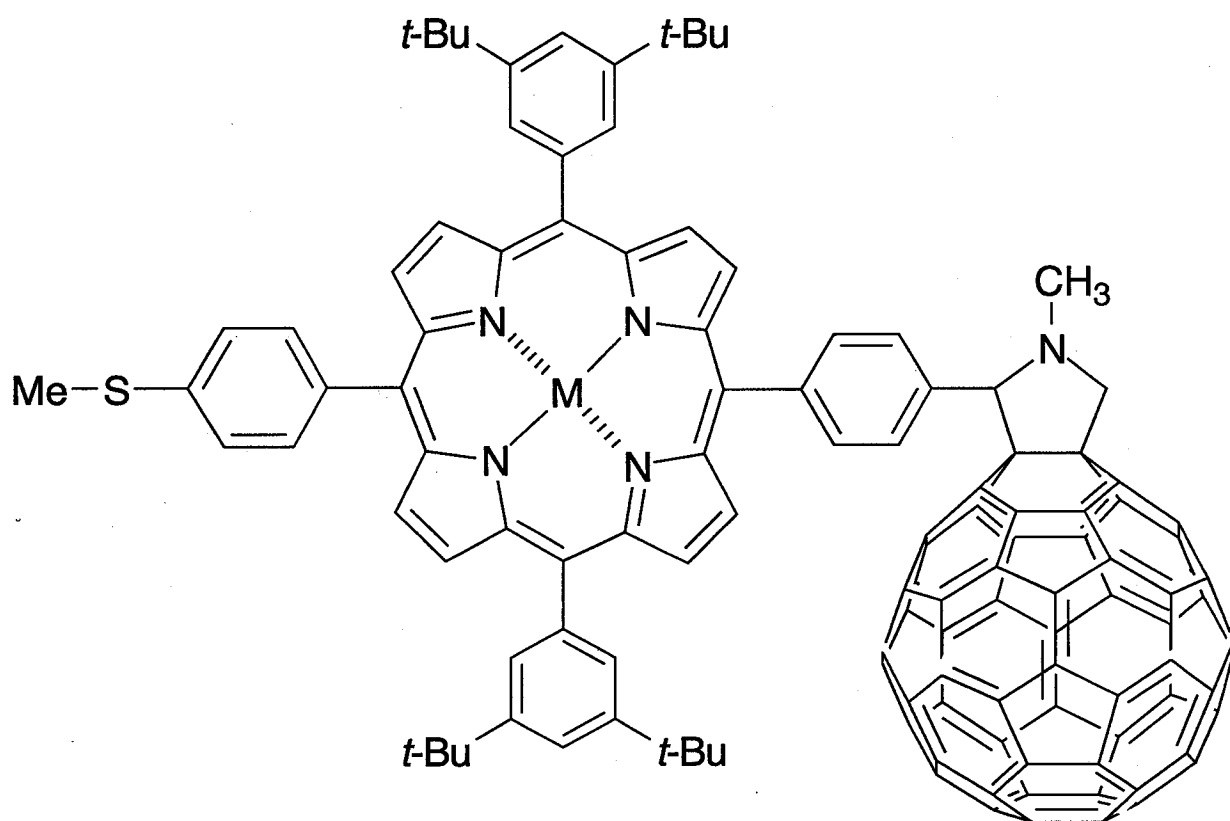


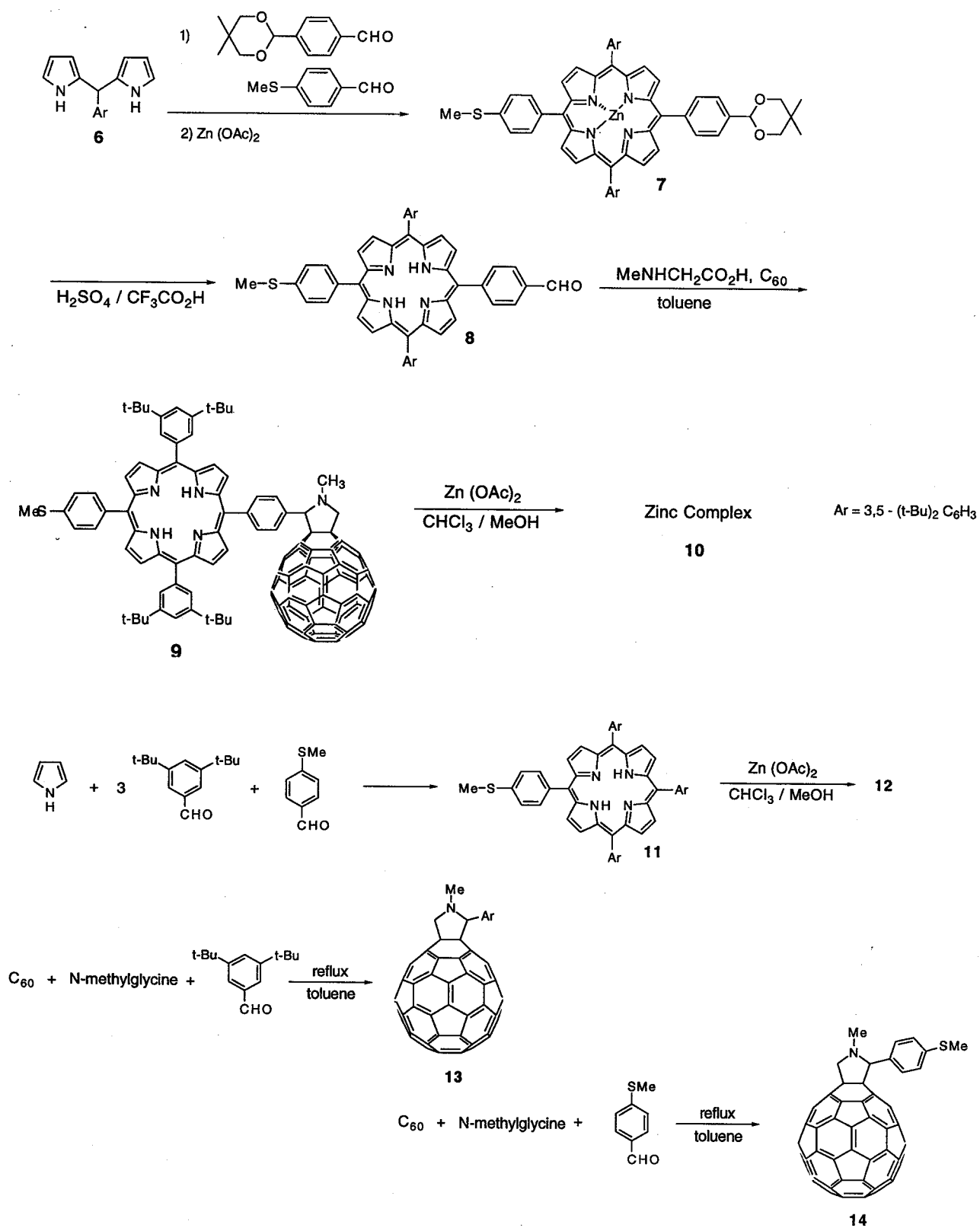
Figure 10 Possible Mechanism of Photocurrent Generation



**9** ( $M = 2\text{H}$ )

**10** ( $M = \text{Zn}$ )

Figure 11 Target Compounds



Scheme 2 Synthesis

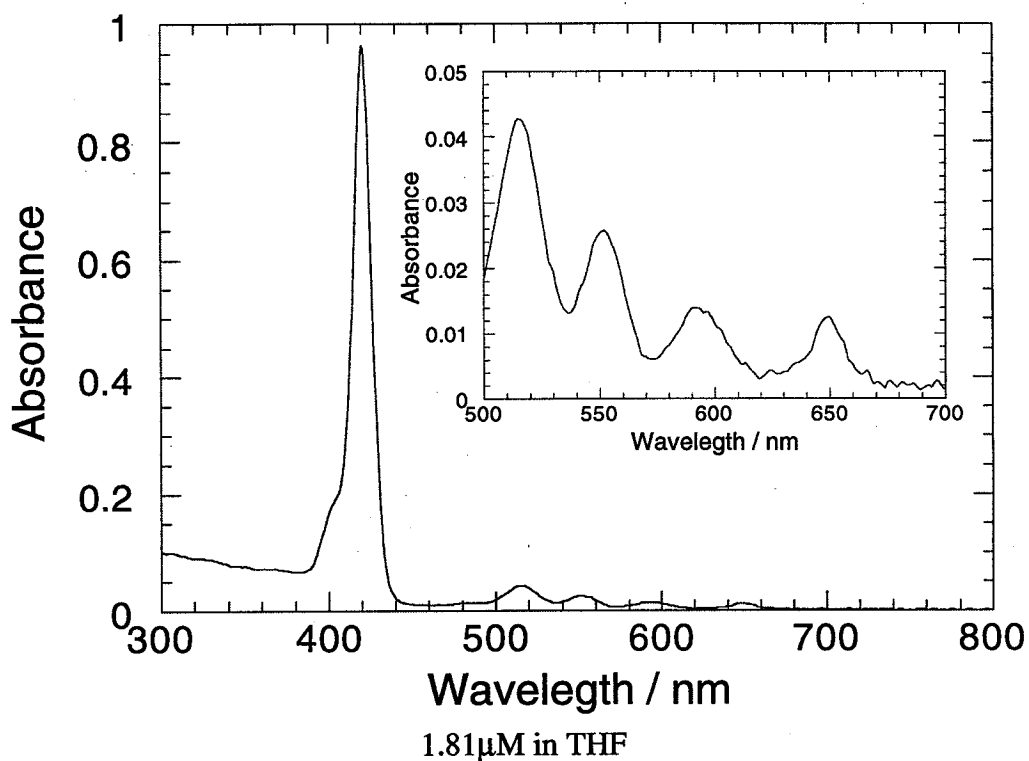


Figure 12 Electronic Absorption Spectra of **9**

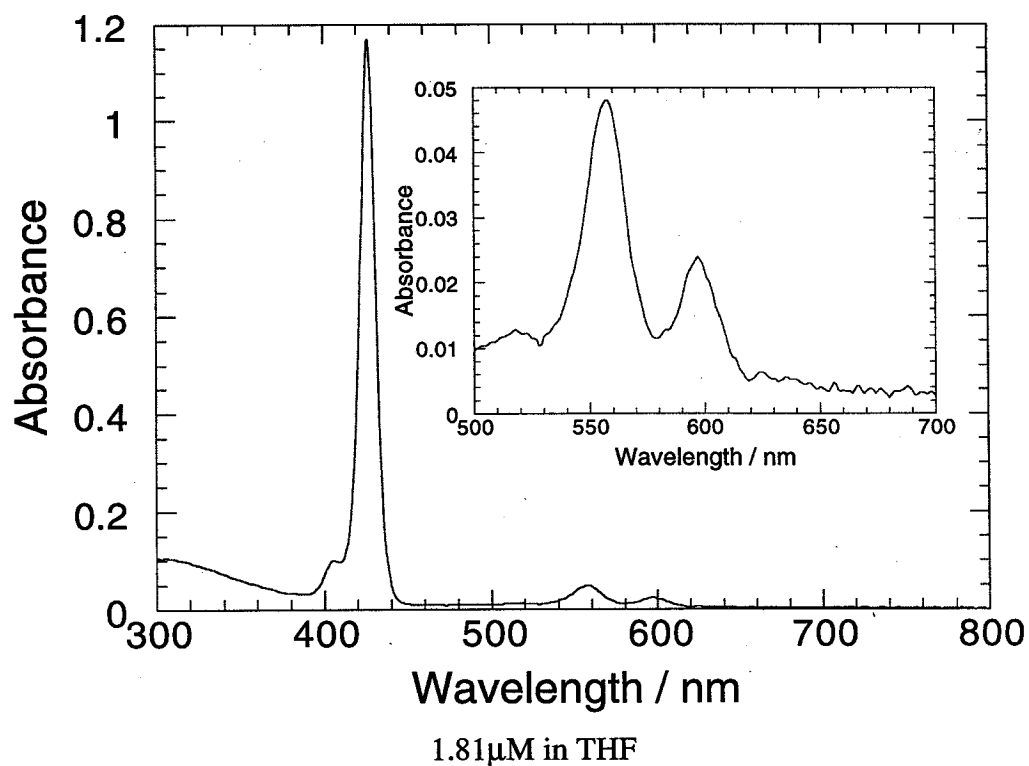


Figure 12-2 Electronic Absorption Spectra of **10**

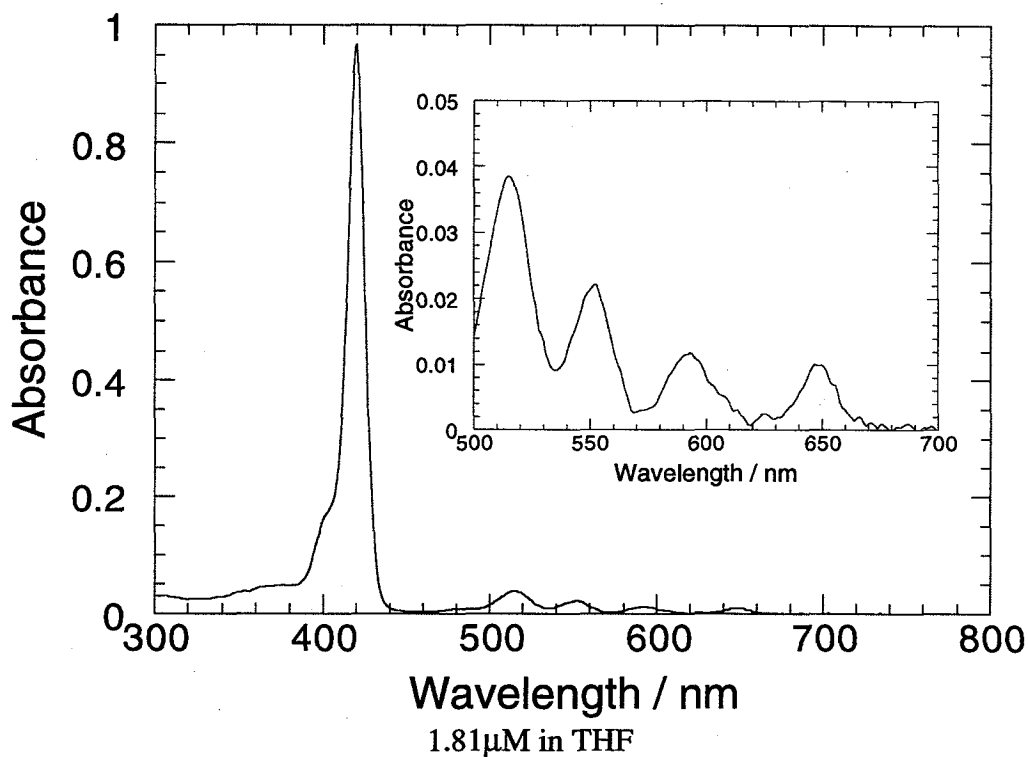


Figure 12-3 Electronic Absorption Spectra of **11**

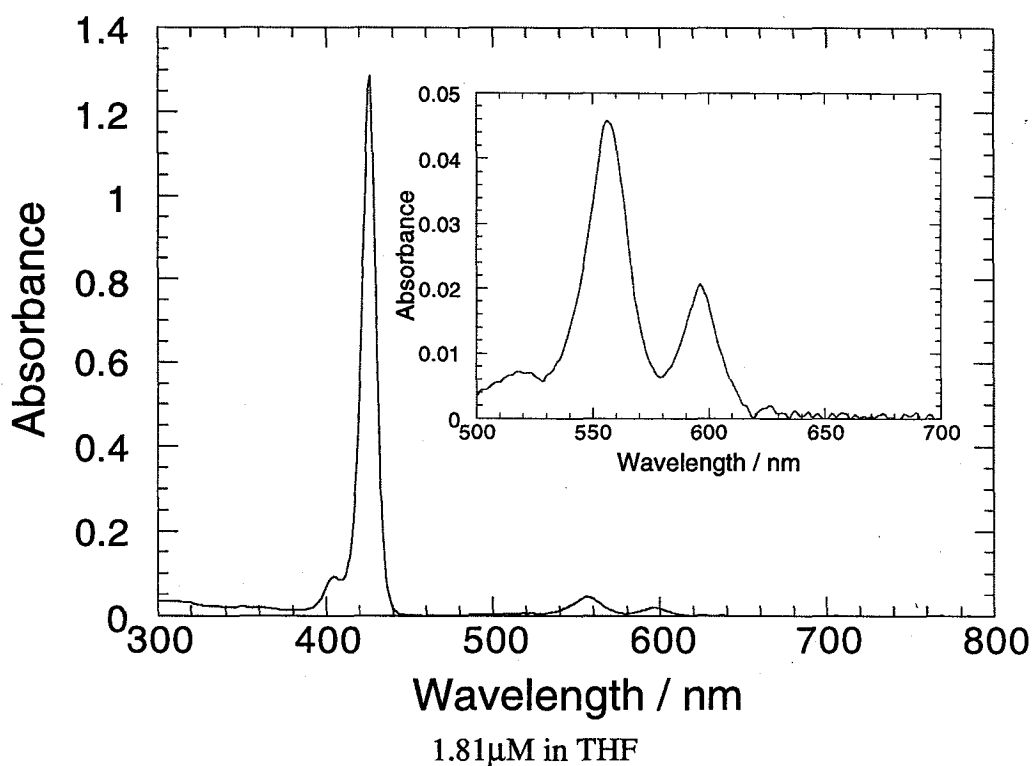
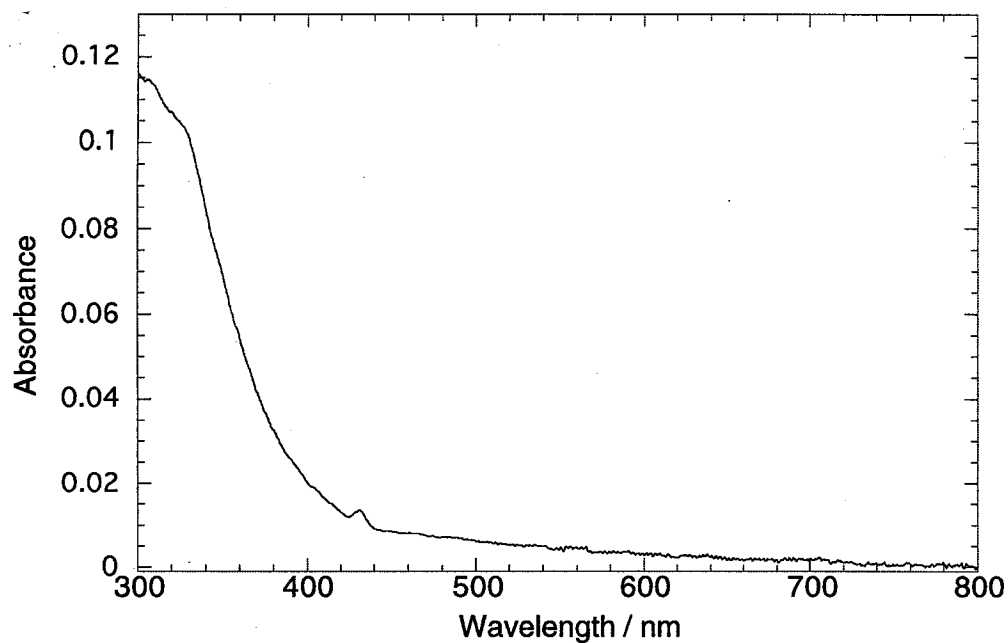


Figure 12-4 Electronic Absorption Spectra of **12**



1.81 $\mu$ M in THF

Figure 12-5 Electronic Absorption Spectra of **13**

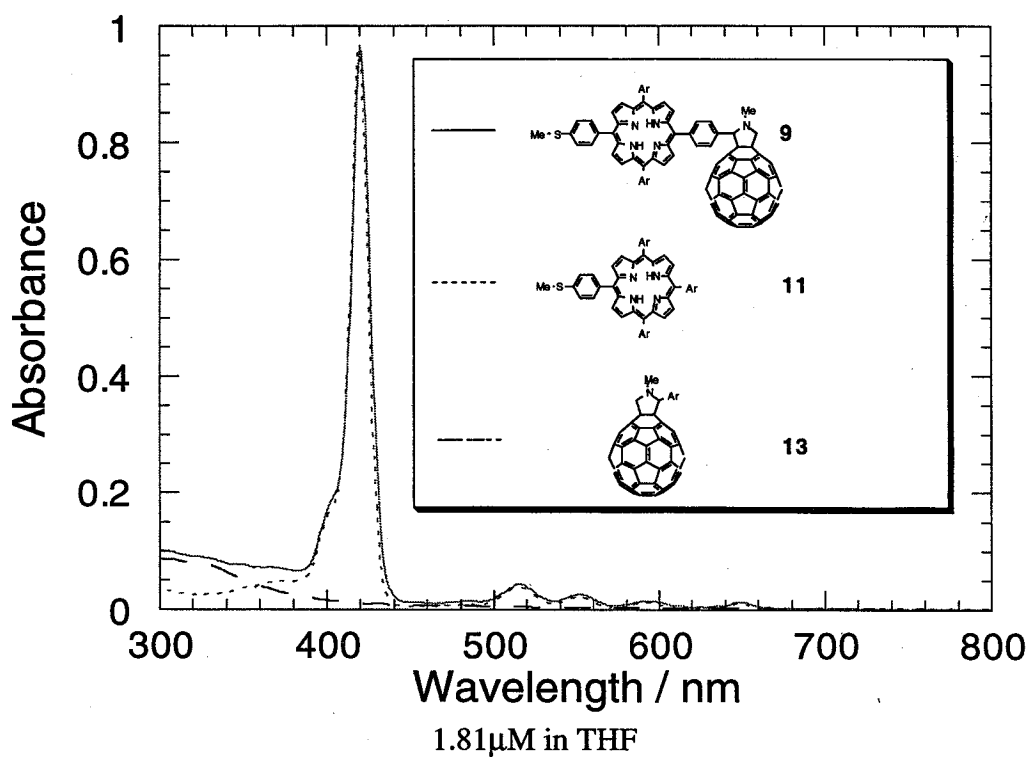
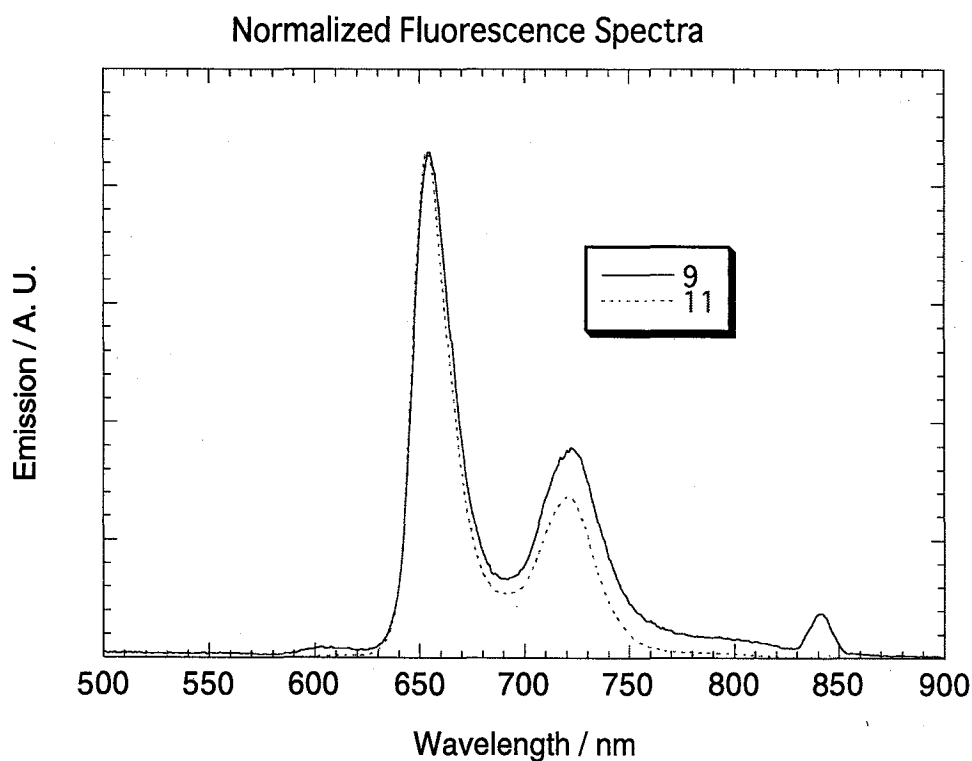
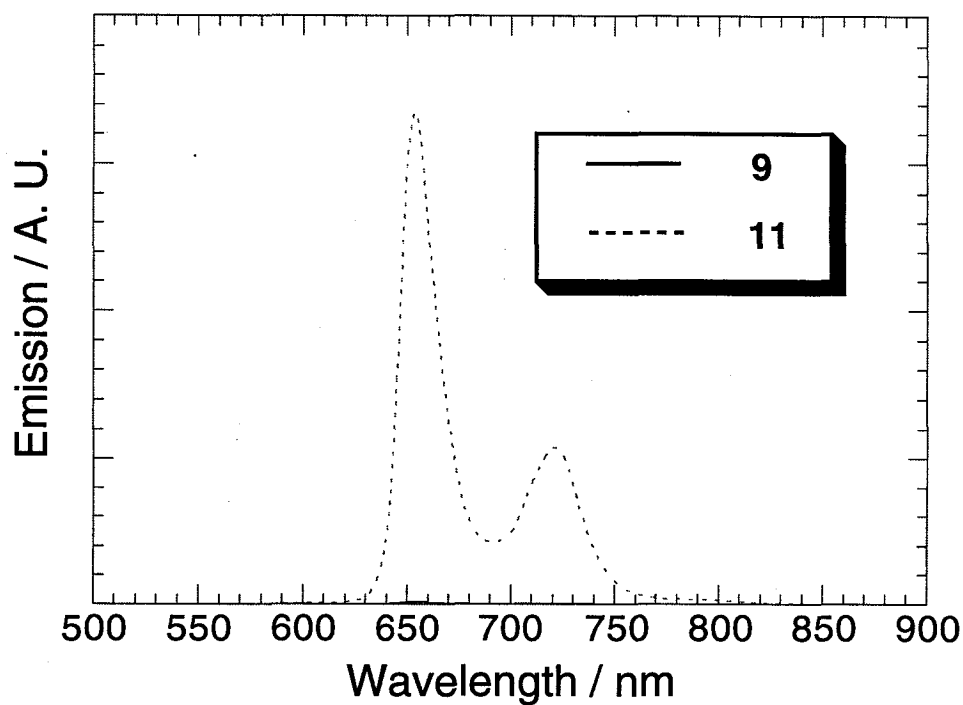


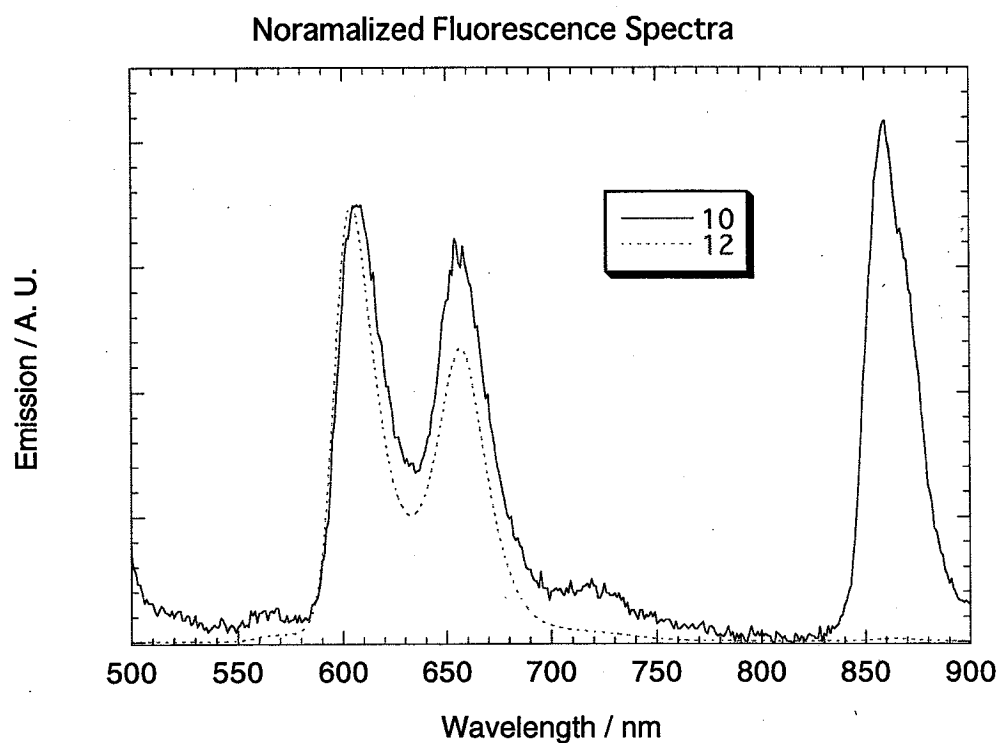
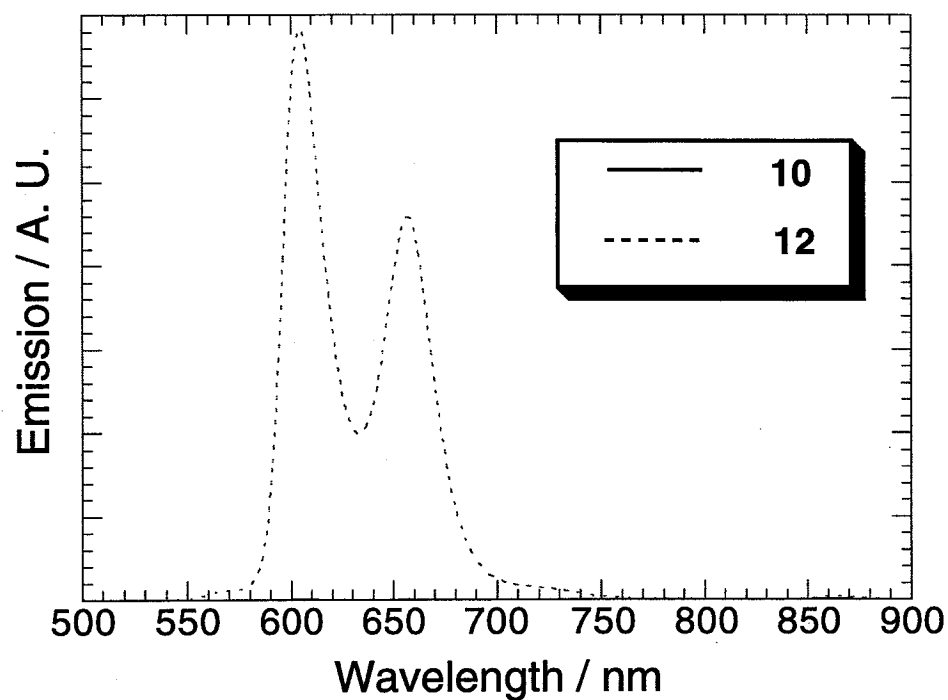
Figure 12-6 Superimposed Electronic Absorption Spectra of **9**, **11**, **13**



1.81  $\mu$ M in THF, Excitation : 420nm

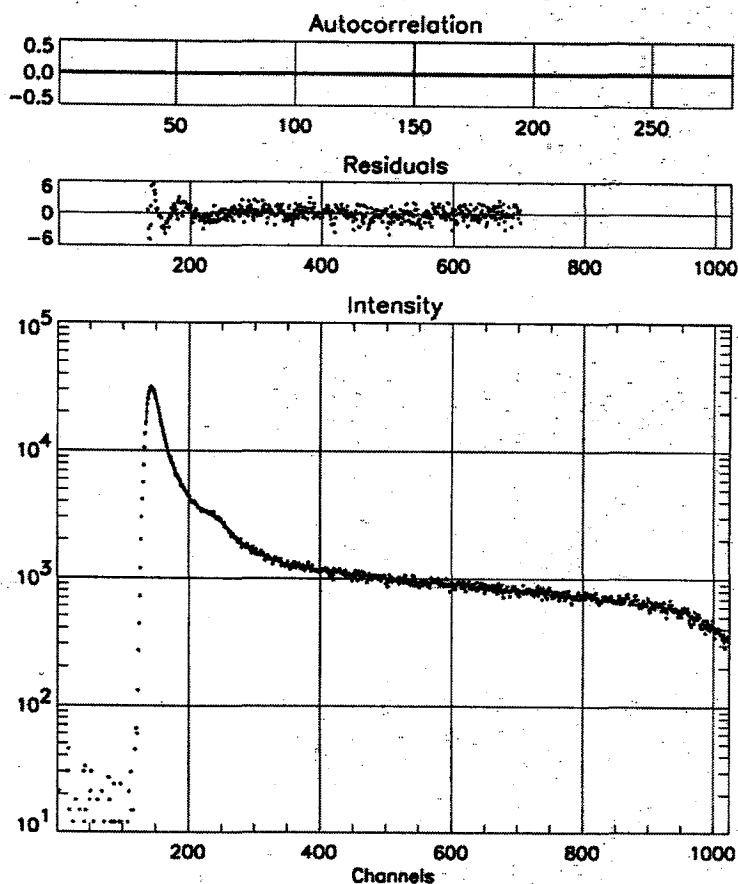
Figure 13 Fluorescence Spectra of **9** and **11**





1.81  $\mu\text{M}$  in THF, Excitation : 427nm

Figure 13-2 Fluorescence Spectra of **10** and **12**

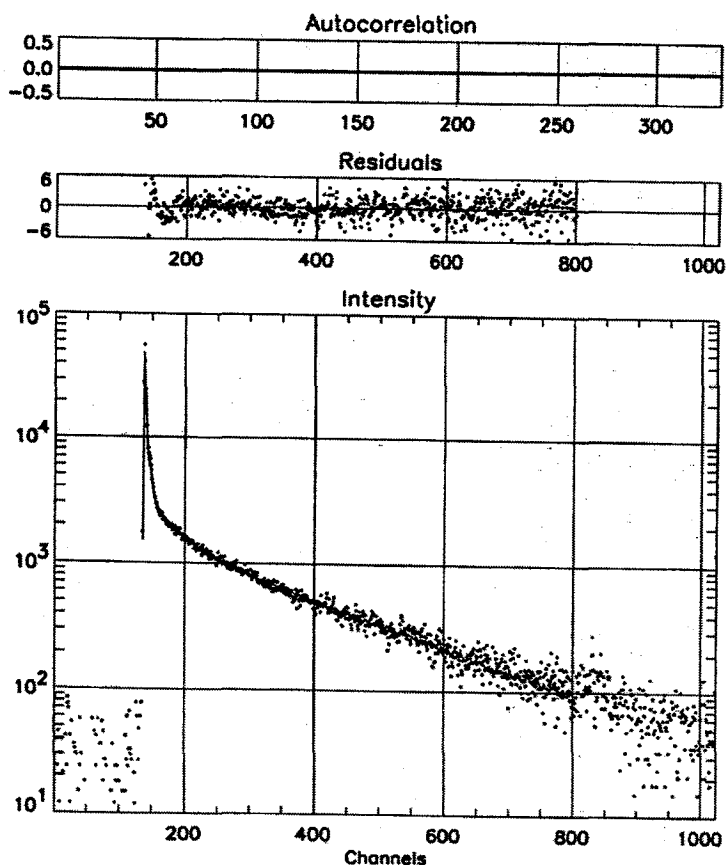


~/chp65.inp  
 compound: C60-DPP(H2)-SMe  
 solvent: THF  
 temp.: 295temperature (C)  
 reference: cr/H2O  
 excitation: 0 (nm)  
 emission: 650 (nm)

3-exponential decay analysis

Shift = 0.0  
 first chan: 133  
 last chan: 701  
 CHISQR = 2.44

$\alpha(1) = 0.468 \pm 0.00$   
 $\tau(1) = 34.9 \pm 0.1$  (ps)  
 $\alpha(2) = 0.081 \pm 0.00$   
 $\tau(2) = 132.4 \pm 0.6$  (ps)  
 $\alpha(3) = 0.010 \pm 0.00$   
 $\tau(3) = 3512.5 \pm 15.8$  (ps)



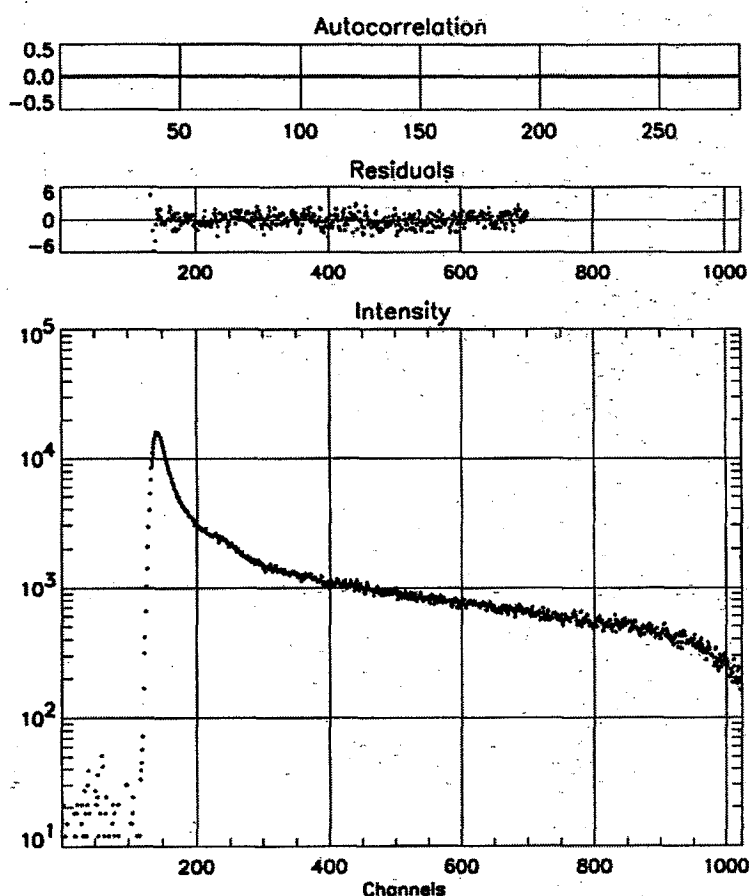
~/chp65d.inp  
 compound: C60-DPP(H2)-SMe  
 solvent: THF  
 temp.: 295temperature (C)  
 reference: crd/H2O  
 excitation: 0 (nm)  
 emission: 650 (nm)

3-exponential decay analysis

Shift = 0.0  
 first chan: 135  
 last chan: 801  
 CHISQR = 5.81

$\alpha(1) = 24.778 \pm 0.00$   
 $\tau(1) = 78.2 \pm 0.0$  (ps)  
 $\alpha(2) = 0.713 \pm 0.00$   
 $\tau(2) = 1226.0 \pm 0.8$  (ps)  
 $\alpha(3) = 0.516 \pm 0.00$   
 $\tau(3) = 8788.0 \pm 1.2$  (ps)

Figure 14 Fluorescence Lifetime Measurement of 9



~/chp72.inp

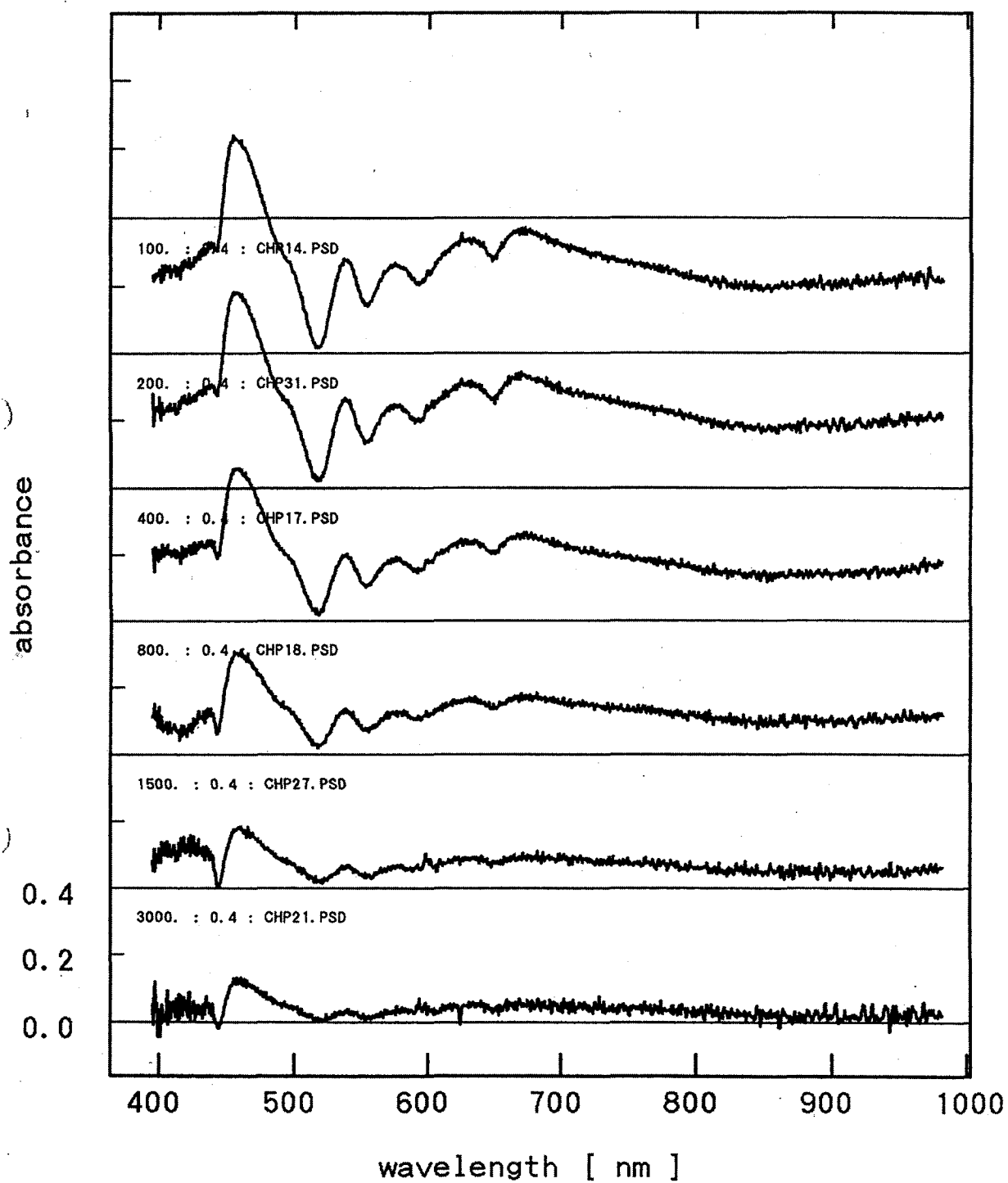
compound: C60-DPP(H2)-SMe  
 solvent: THF  
 temp.: 295 (C)  
 reference: cr/h2o  
 excitation: 400 (nm)  
 emission: 720 (nm)

3-exponential decay analysis

Shift = 0.8  
 first chan: 133  
 last chan: 701  
 CHISQR = 2.00

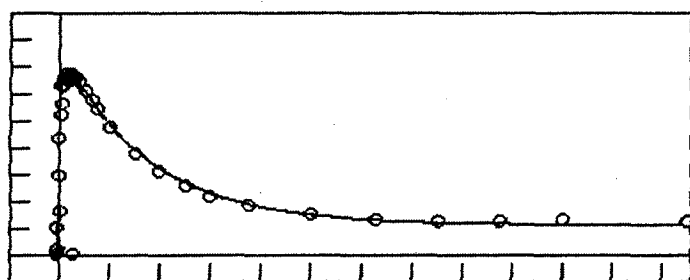
$a(1) = 0.276 \pm 0.00$   
 $\tau(1) = 24.4 \pm 0.1$  (ps)  
 $a(2) = 0.012 \pm 0.00$   
 $\tau(2) = 2155.2 \pm 5.6$  (ps)  
 $a(3) = 0.055 \pm 0.00$   
 $\tau(3) = 120.6 \pm 0.6$  (ps)

Figure 14-2 Fluorescence Lifetime Measurement of 9

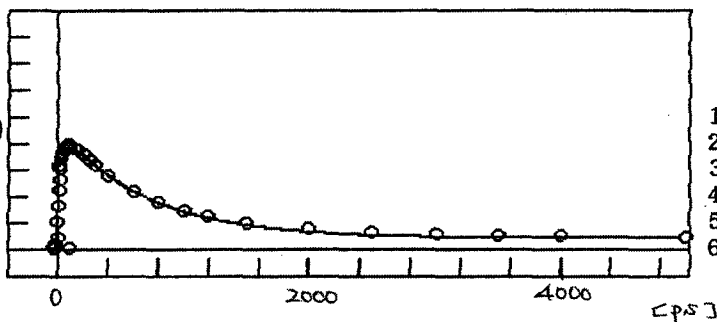


21 30 06-02-'96 00:38  
CHP14.prn

Figure 14-3 Time-Resolved Transient Absorption Spectra of **9**



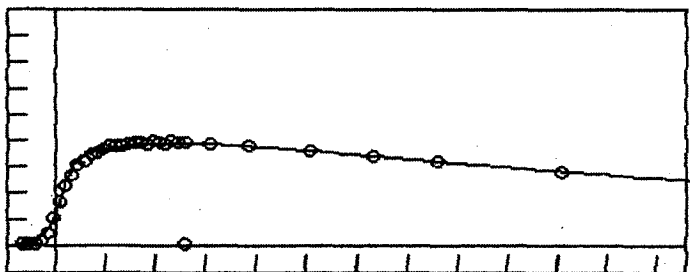
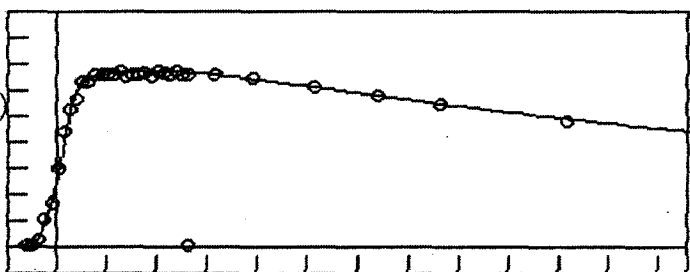
<1> CHP.460  
 1:PRE-EXP. FACTOR (A) .68  
 2:PRE-EXP. FACTOR (B) -.20  
 3:DECAY TIME (T1 / ps) 700.0  
 4:DECAY TIME (T2 / ps) 50.0  
 5:CONST. COMPONENT (C) .11  
 6:0 point shift 6.00  
 FULL ABS SCALE 1.00  
 FULL TIME SCALE 500.0



<2> CHP.675  
 1:PRE-EXP. FACTOR (A) .43  
 2:PRE-EXP. FACTOR (B) -.18  
 3:DECAY TIME (T1 / ps) 700.0  
 4:DECAY TIME (T2 / ps) 50.0  
 5:CONST. COMPONENT (C) .04  
 6:0 point shift 3.28  
 FULL ABS SCALE 1.00  
 FULL TIME SCALE 500.0

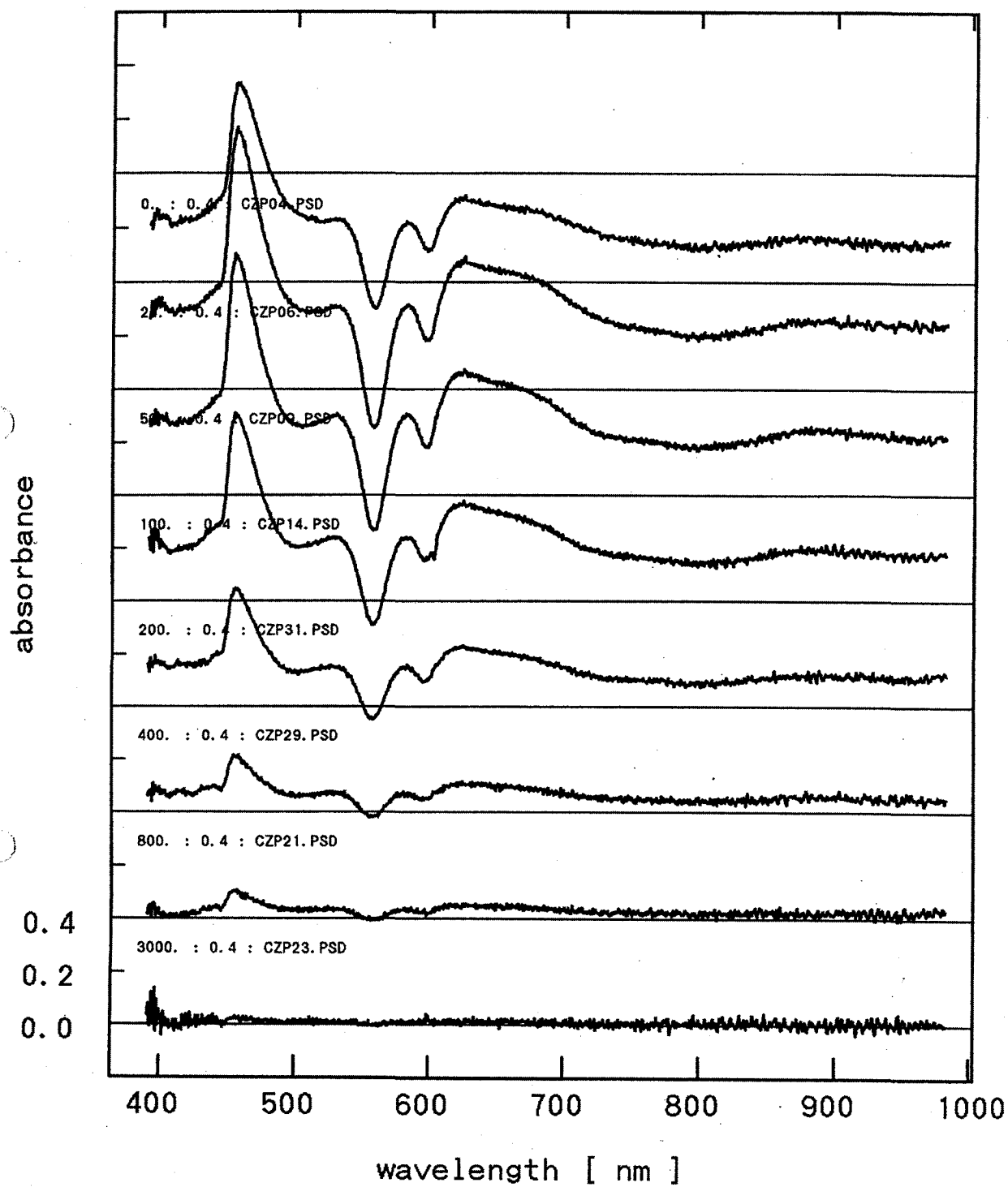
DO YOU WANT CHANGE PARAMATER(S)?  
 (Y / N ) ?

C1 CU CA S1 SU VOID NWL INS REP HIST



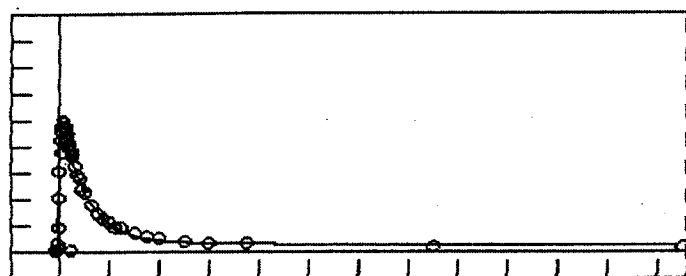
[ps]

Figure 14-4 Analysis of Time-Resolved Transient Absorption Spectra of 9

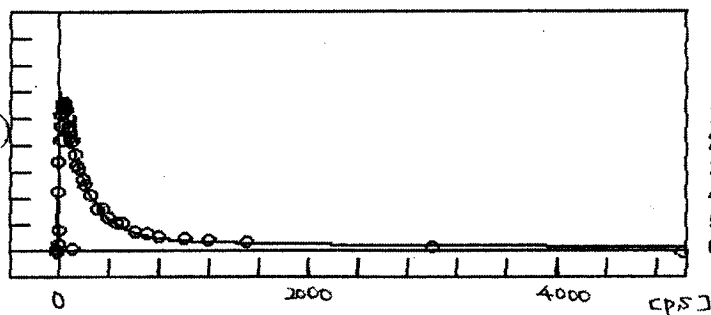


21 30 06-02-'96 01:35  
C2P04.prn

Figure 14-5 Time-Resolved Transient Absorption Spectra of 10



<1> CZP.650  
 1:PRE-EXP. FACTOR (A) .54  
 2:PRE-EXP. FACTOR (B) .02  
 3:DECAY TIME (T1 / ps) 200.0  
 4:DECAY TIME (T2 / ps) 1600.0  
 5:CONST. COMPORNENT (C) .02  
 6:0 point shift 3.00  
 FULL ABS SCALE 1.00  
 FULL TIME SCALE 500.0



<2> CZP.900  
 1:PRE-EXP. FACTOR (A) .62  
 2:PRE-EXP. FACTOR (B) .04  
 3:DECAY TIME (T1 / ps) 200.0  
 4:DECAY TIME (T2 / ps) 1600.0  
 5:CONST. COMPORNENT (C) .01  
 6:0 point shift 7.70  
 FULL ABS SCALE .50  
 FULL TIME SCALE 500.0

DO YOU WANT CHANGE PARAMATER(S)?  
 (Y / N ) ?

C1 CU CA S1 SU VOID NWL INS REP HIST

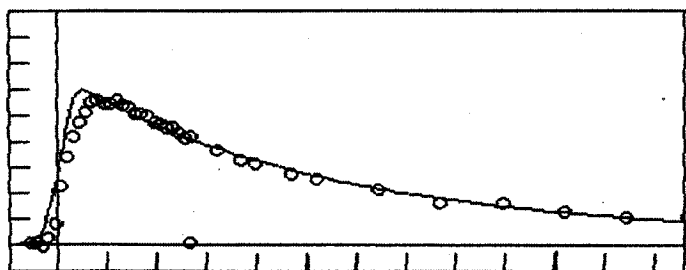
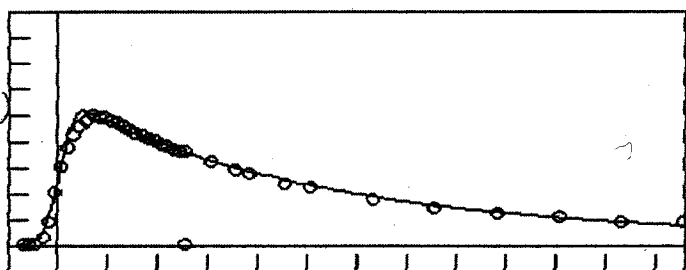
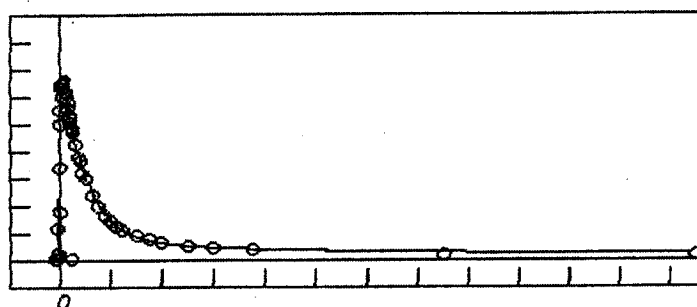
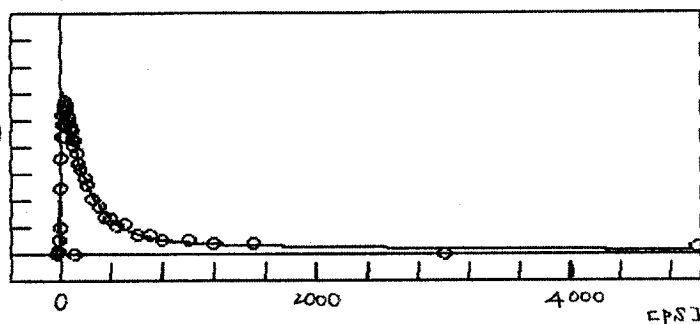


Figure 14-6 Analysis of Time-Resolved Transient Absorption Spectra of 10



<1> CZP.460  
 1:PRE-EXP. FACTOR (A) .69  
 2:PRE-EXP. FACTOR (B) .05  
 3:DECAY TIME (T1 / ps) 200.0  
 4:DECAY TIME (T2 / ps) 1600.0  
 5:CONST. COMPONENT (C) .02  
 6:0 point shift 3.00  
 FULL ABS SCALE 1.50  
 FULL TIME SCALE 500.0



<2> CZP.879  
 1:PRE-EXP. FACTOR (A) .62  
 2:PRE-EXP. FACTOR (B) .05  
 3:DECAY TIME (T1 / ps) 200.0  
 4:DECAY TIME (T2 / ps) 1600.0  
 5:CONST. COMPONENT (C) .01  
 6:0 point shift 5.20  
 FULL ABS SCALE .50  
 FULL TIME SCALE 500.0

DO YOU WANT CHANGE PARAMETER(S)?  
 (Y / N) ?

C1 CU CA S1 SU VOID NWL INS REP HIST

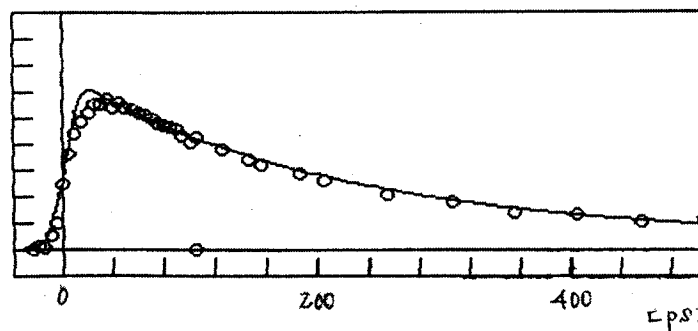
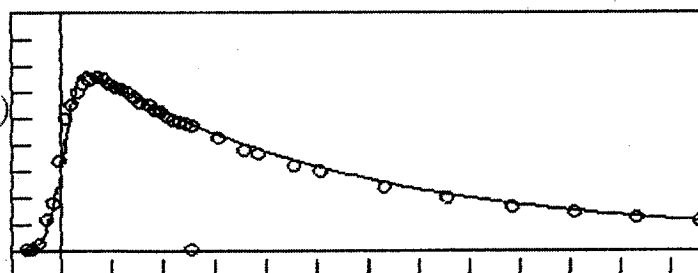
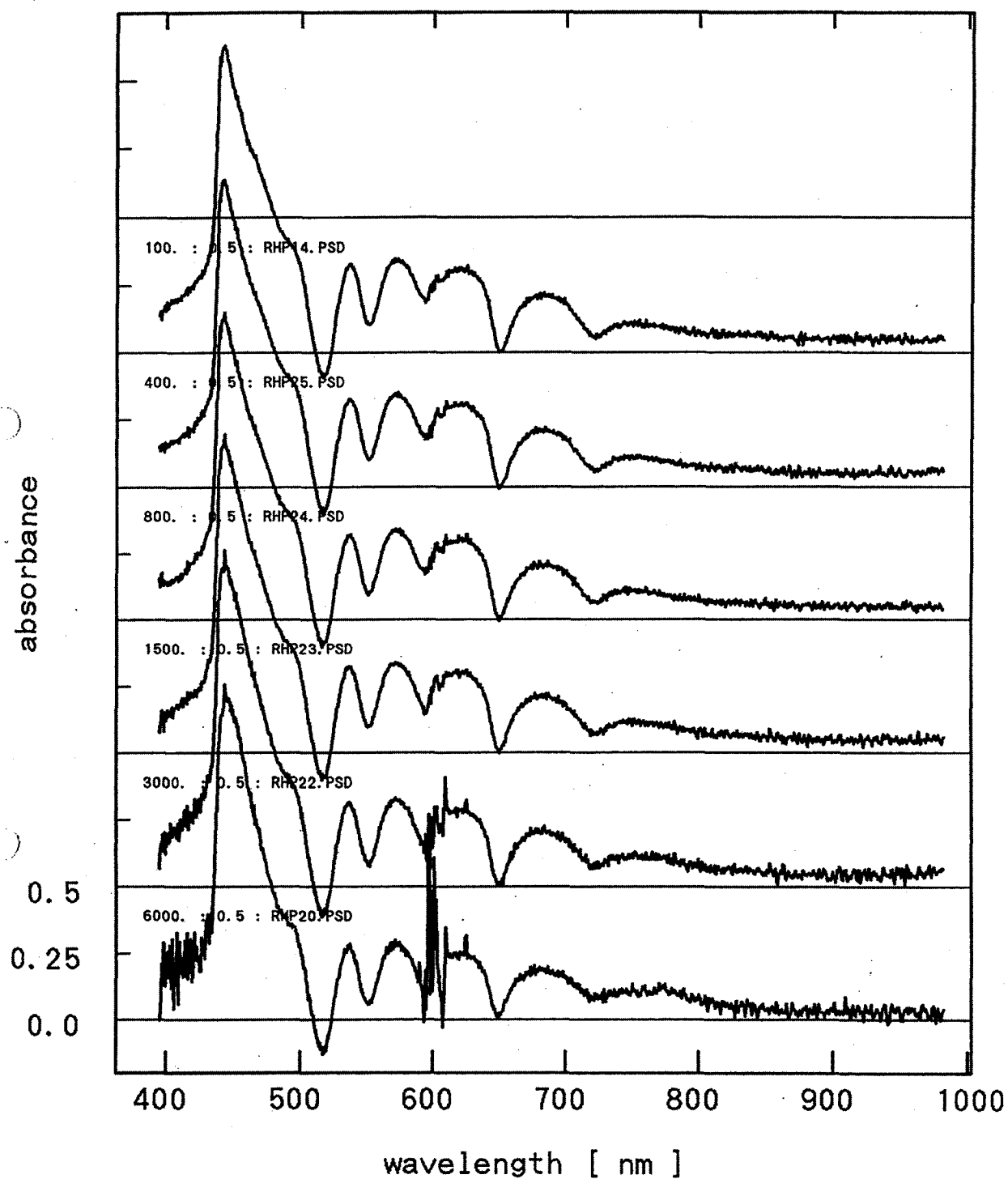


Figure 14-7 Analysis of Time-Resolved Transient Absorption Spectra of 10





21 30 06-02-'96 02:06  
RHP14.prn

Figure 14-8 Time-Resolved Transient Absorption Spectra of 11

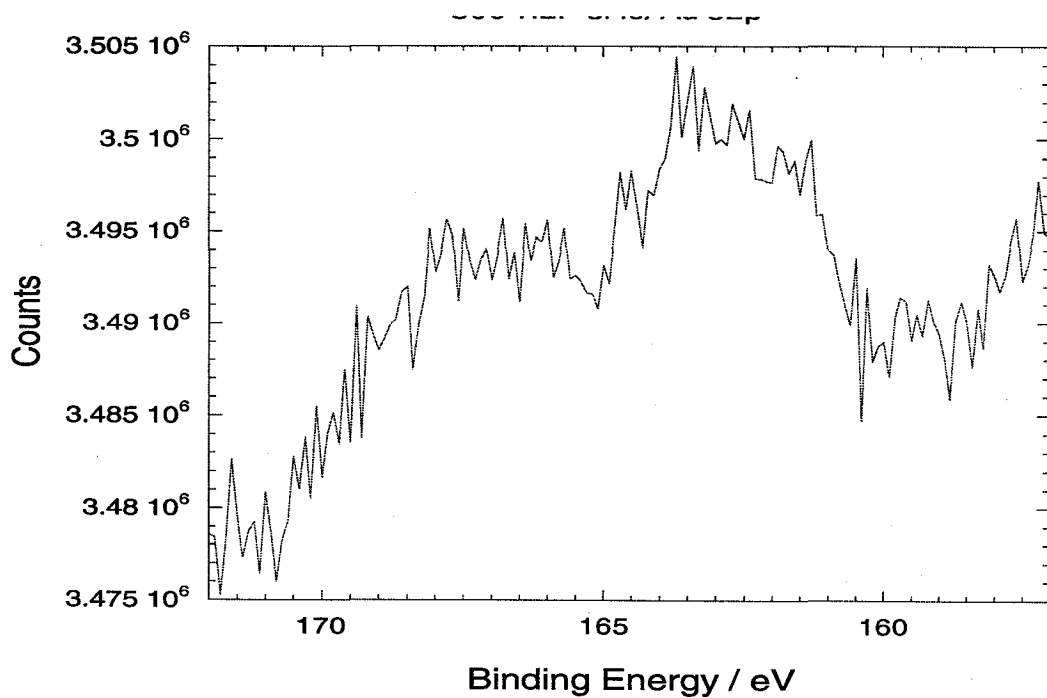
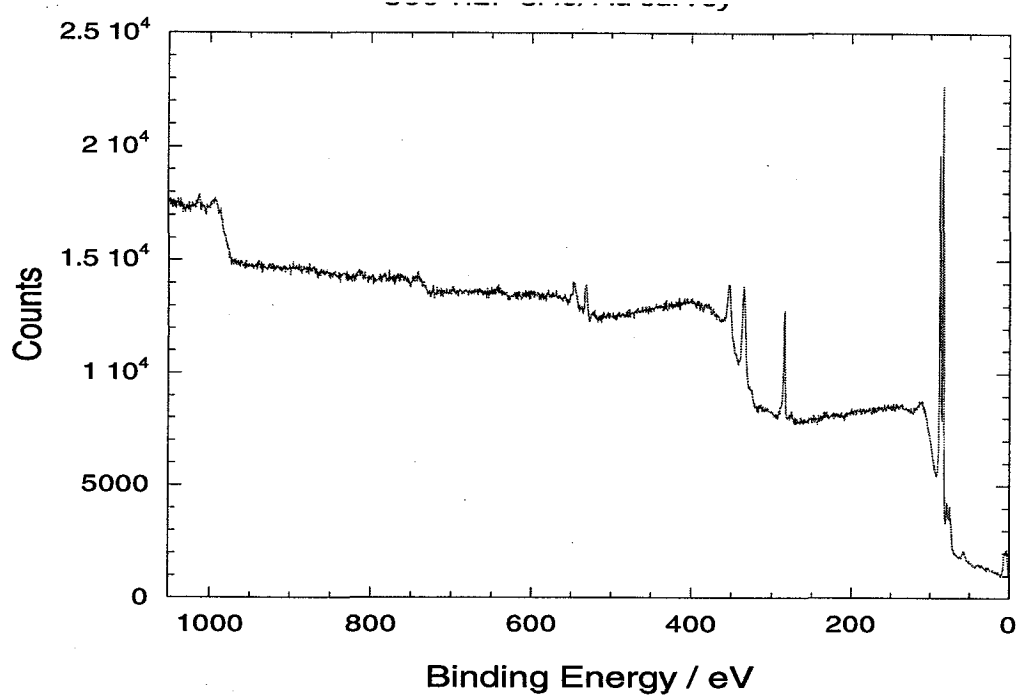


Figure 15 X-ray Photoelectron Spectra of **9** / Au

# X-ray Photoelectron Spectroscopy

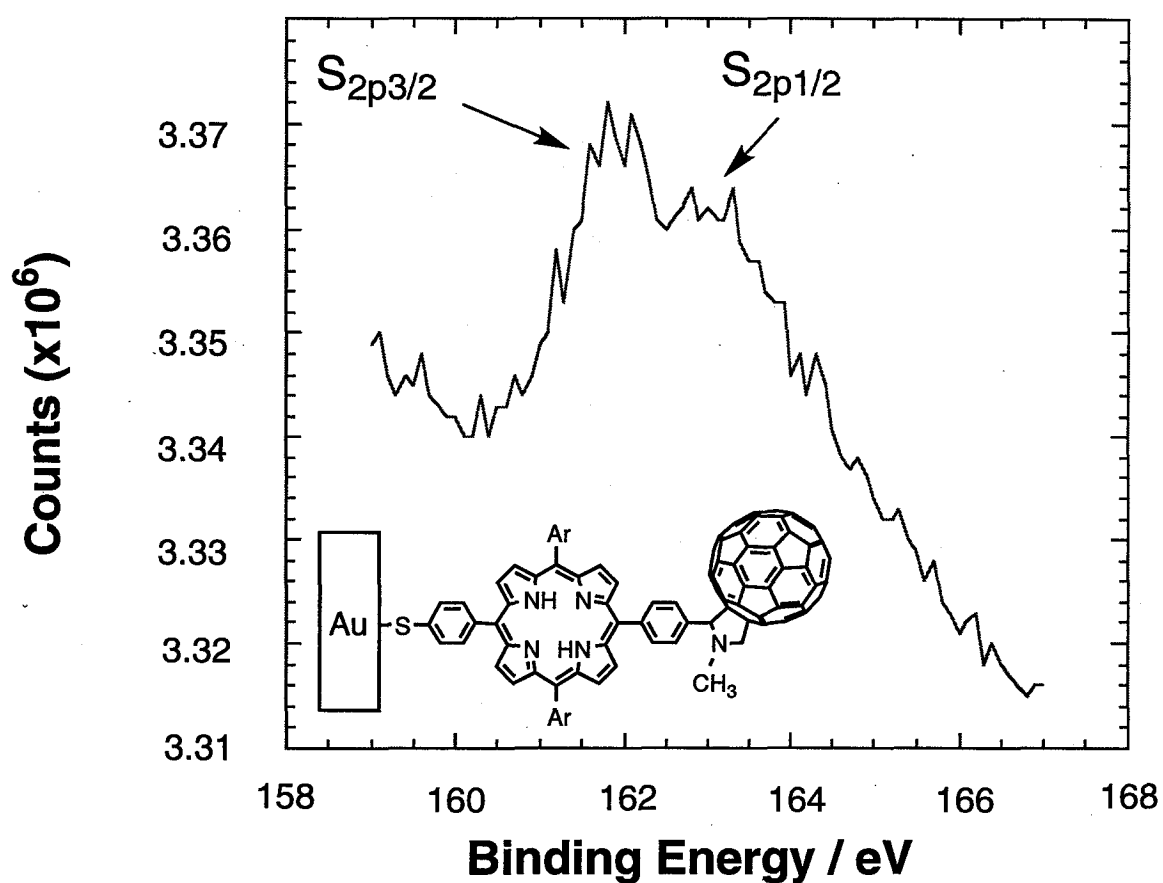


Figure 15-2 X-ray Photoelectron Spectra of **9** / Au

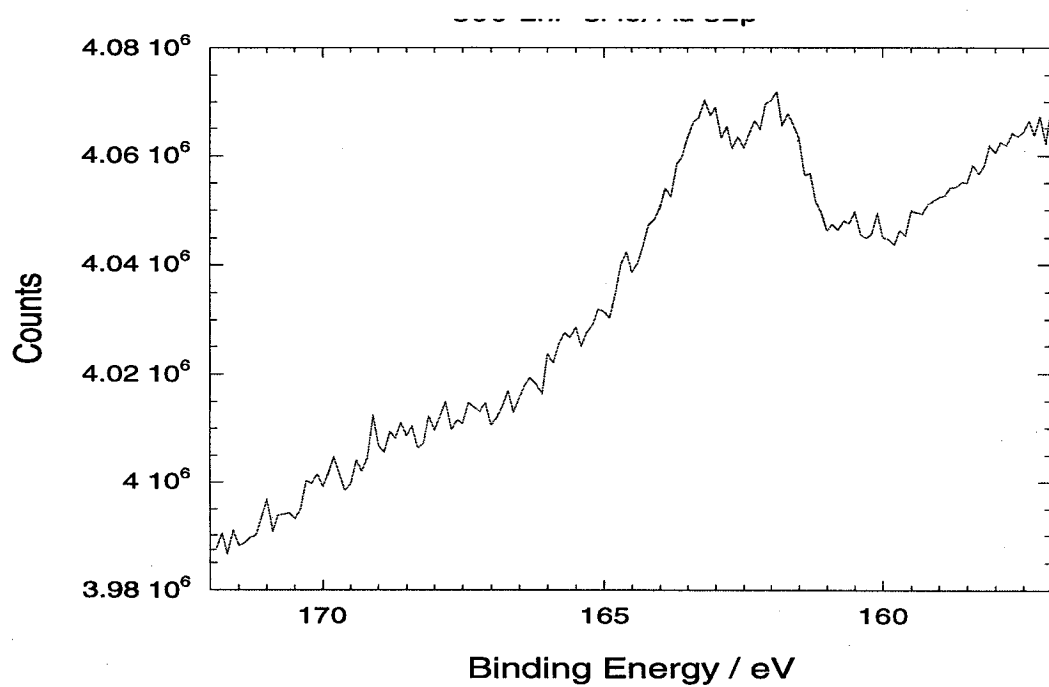
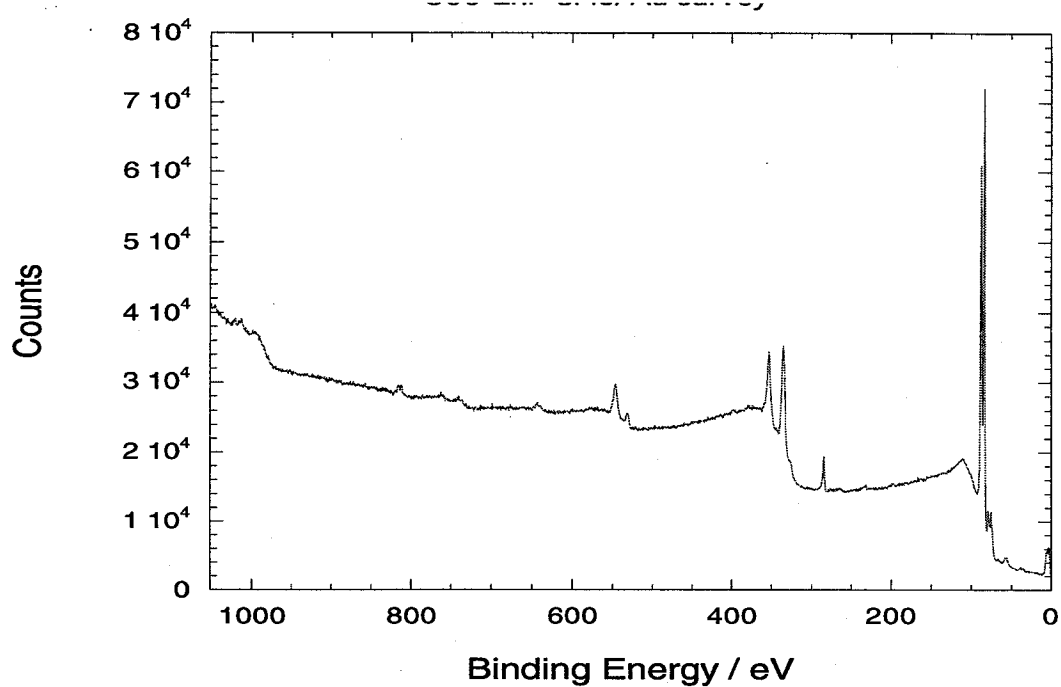


Figure 15-3 X-ray Photoelectron Spectra of **10** / Au

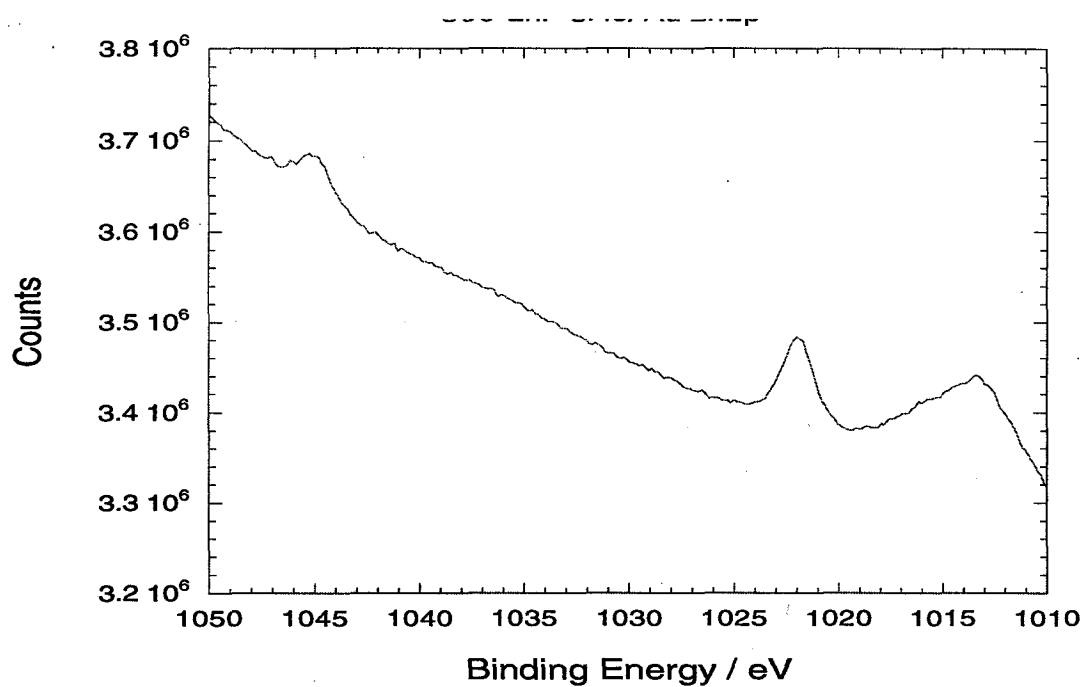
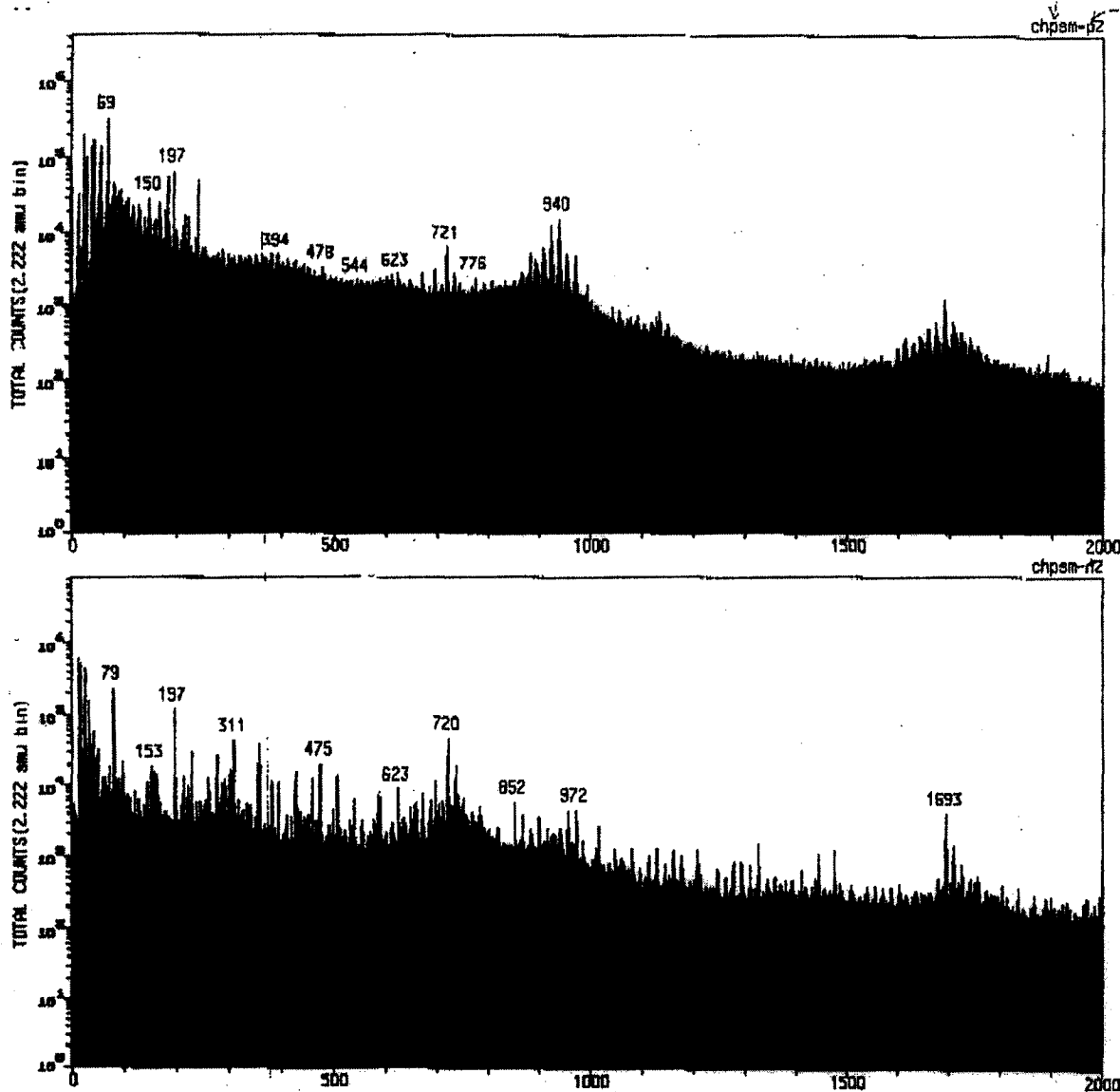


Figure 15-4 X-ray Photoelectron Spectra of **10** / Au



FILE NAME: chpm-p2 DATE : 1 Nov 96 11:04 ACQUISITION TIME: 6.0 MIN. TOTAL INTEGRAL : 4192768

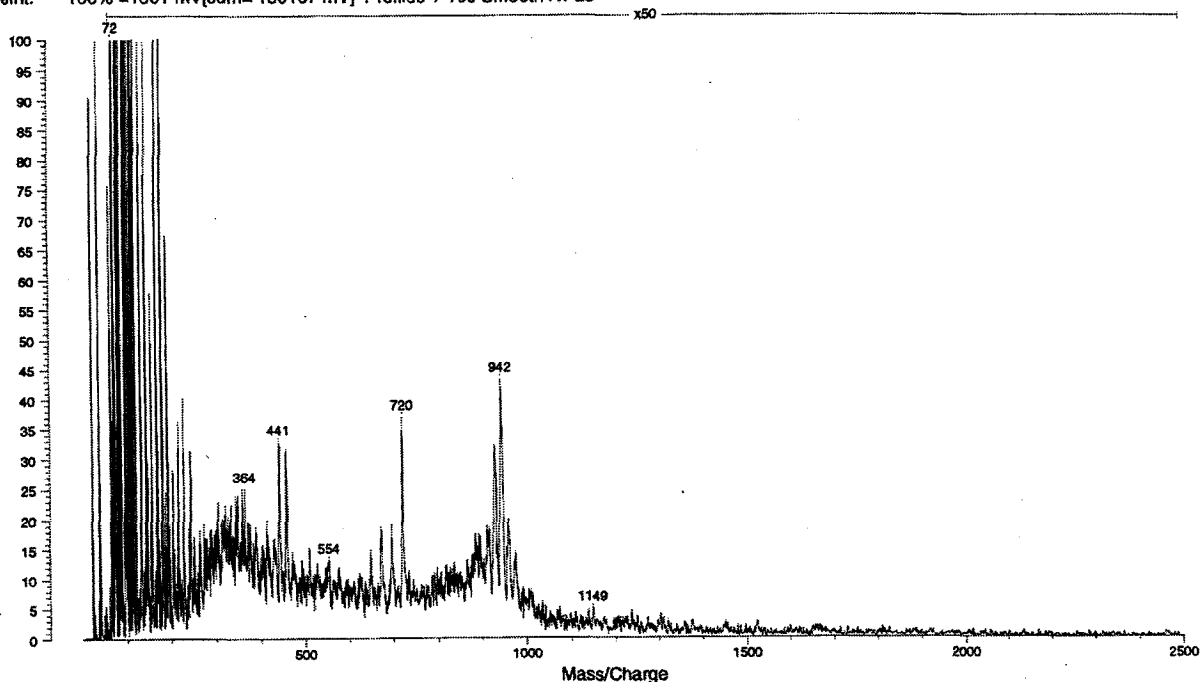
+ IONS PRIMARY GUN: LMIG TIME RECORDER: 1-Stop TDC X-Y SOURCE: Raster TIME PER CHANNEL: 156 ps  
DATA SET: 1 Spectra; 0 Image(s) RASTER SIZE: 81µm RASTER TYPE: Full HI Flyback

FILE NAME: chpm-r2 DATE : 1 Nov 96 10:44 ACQUISITION TIME: 6.0 MIN. TOTAL INTEGRAL : 5168128

- IONS PRIMARY GUN: LMIG TIME RECORDER: 1-Stop TDC X-Y SOURCE: Raster TIME PER CHANNEL: 156 ps  
DATA SET: 1 Spectra; 0 Image(s) RASTER SIZE: 81µm RASTER TYPE: Full HI Flyback

Figure 16 Ga<sup>+</sup> Ionization TOF Mass Spectra of 9 / Au

C60-H2P-SMe/Au  
 Data: C600006.3 18 Dec 96 14:29 Cal: sanken 18 Dec 96 14:32  
 Kratos Kompact MALDI 4 V5.2.0: + Linear Low Power: 120  
 %Int. 100% =1501 mV[sum= 150107 mV] Profiles 1-100 Smooth Av 25



C60-H2P-SMe/Au  
 Data: C600001.3 18 Dec 96 14:17 Cal: sanken 18 Dec 96 14:15  
 Kratos Kompact MALDI 4 V5.2.0: - Linear Low Power: 80  
 %Int. 100% =329 mV[sum= 32950 mV] Profiles 1-100 Smooth Av 25

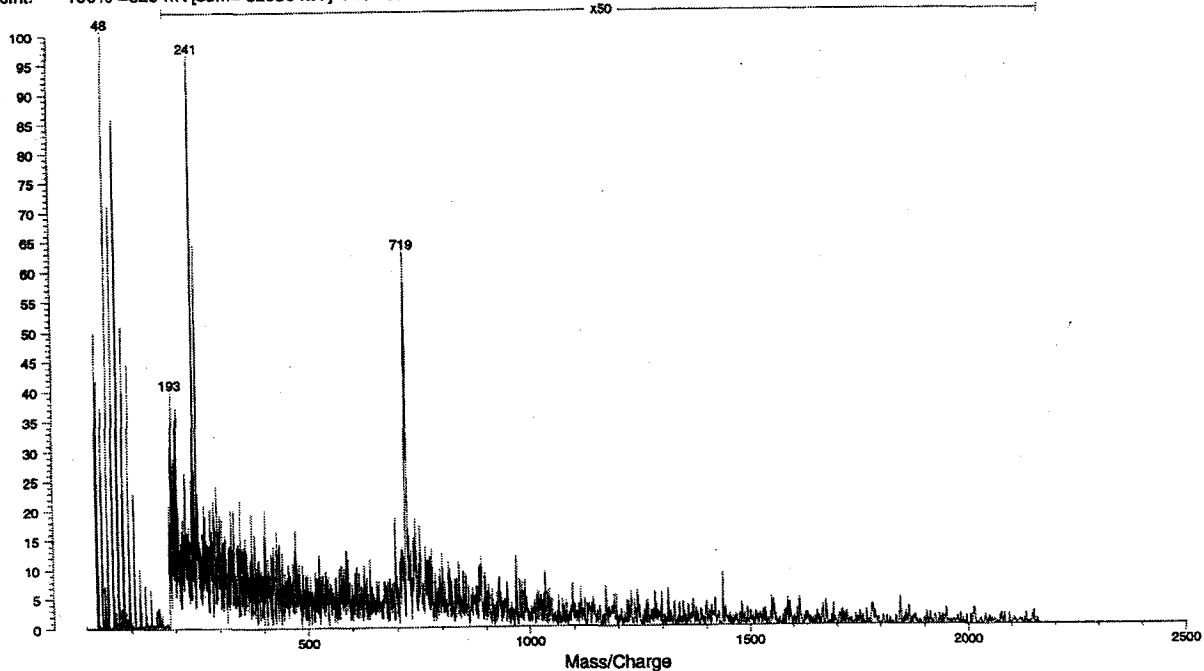
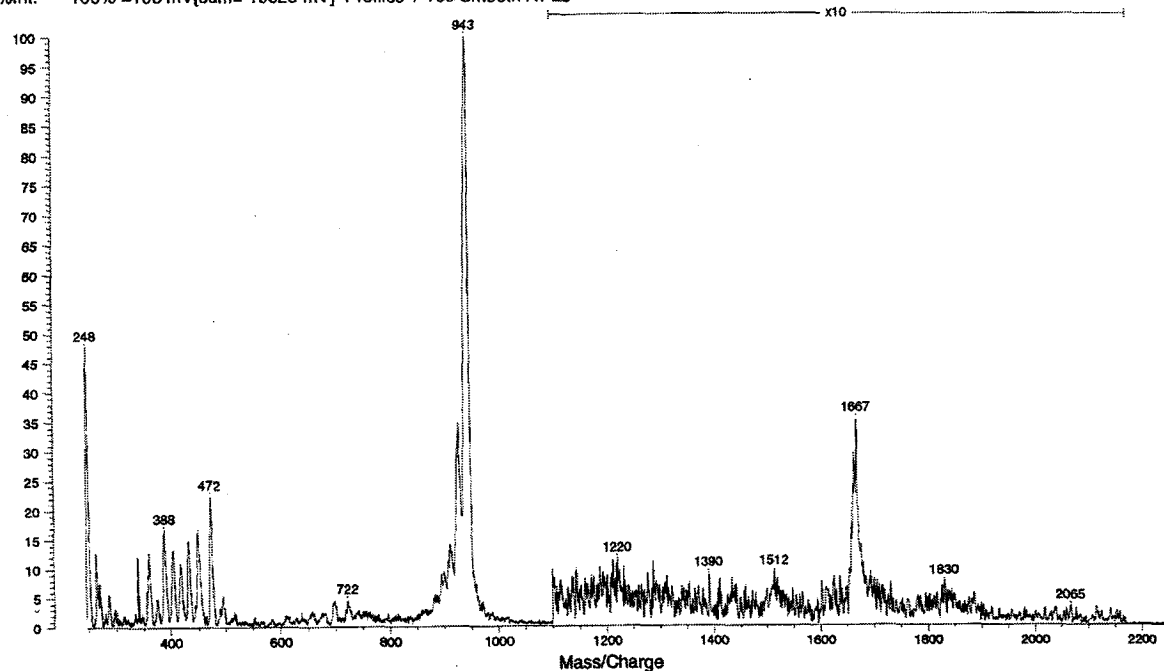


Figure 17 Laser Ionization TOF Mass Spectra of **9** / Au

C60-H2P-SMe/S  
 Data: C600015.8 18 Dec 96 15:54 Cal: tof-IDE 18 Dec 96 13:32  
 Kratos Kompact MALDI 4 V5.2.0: + Linear Low Power: 43  
 %Int. 100% =106 mV[sum= 10625 mV] Profiles 1-100 Smooth Av 25



C60-H2P-SMe  
 Data: C600008.5 18 Dec 96 14:55 Cal: tof-IDE 23 Nov 96 13:48  
 Kratos Kompact MALDI 4 V5.2.0: - Linear Low Power: 58  
 %Int. 100% =1000 mV[sum= 100027 mV] Profiles 1-100 Smooth Av 25

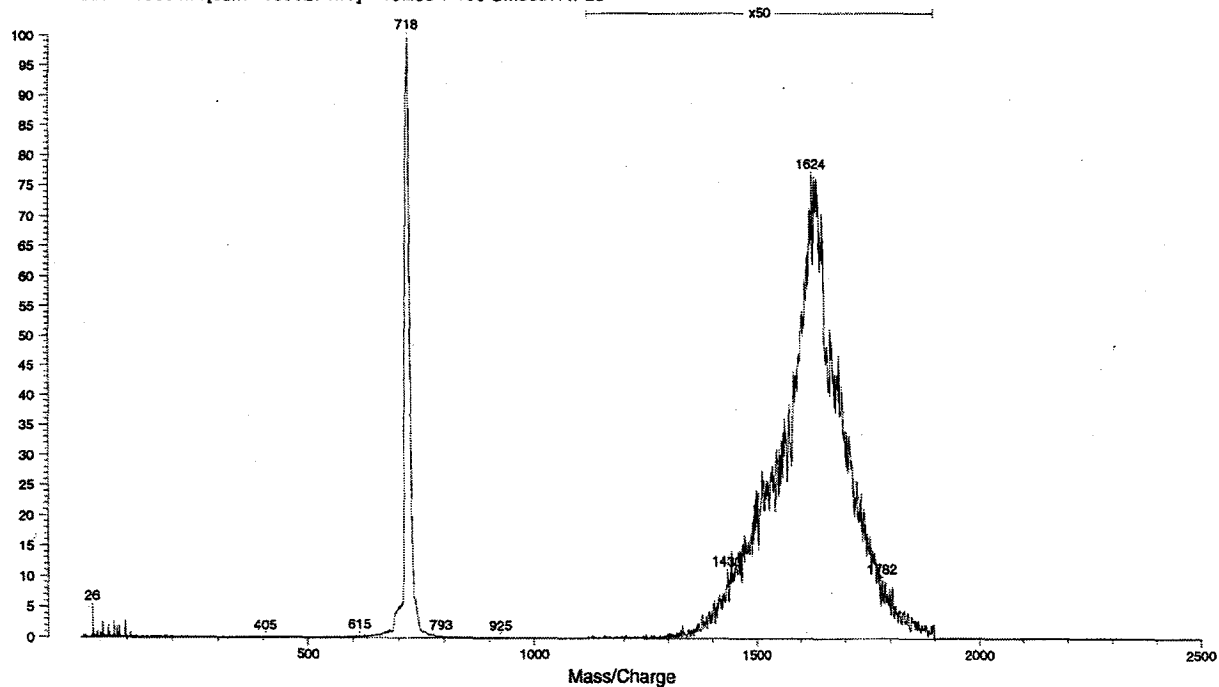


Figure 17-2 Laser Ionization TOF Mass Spectra of **9**  
 without Matrix



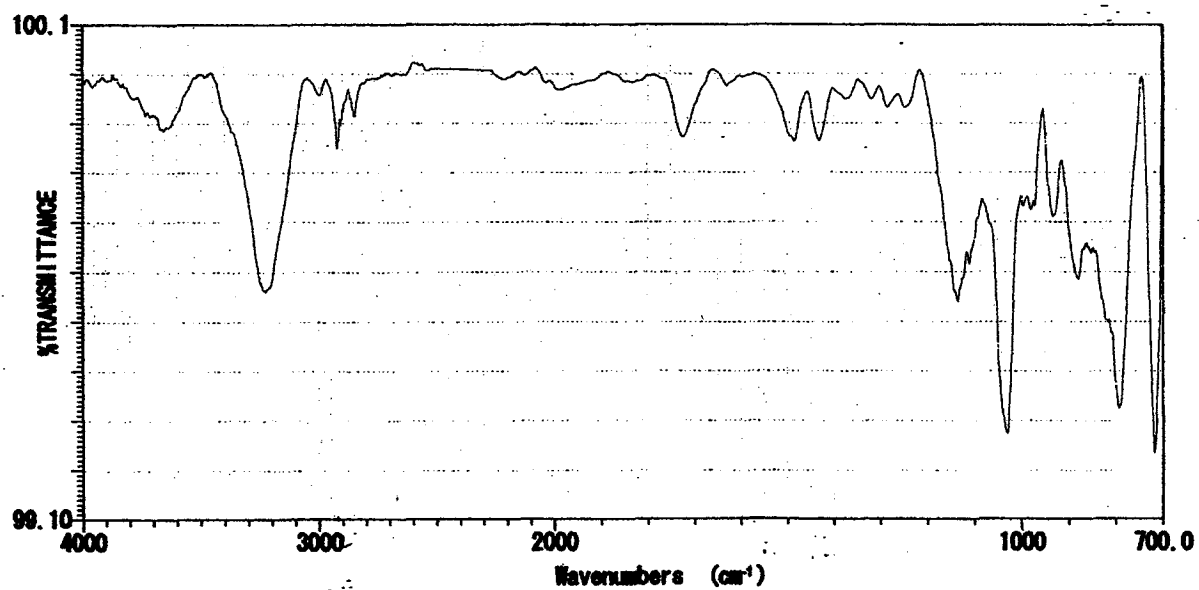
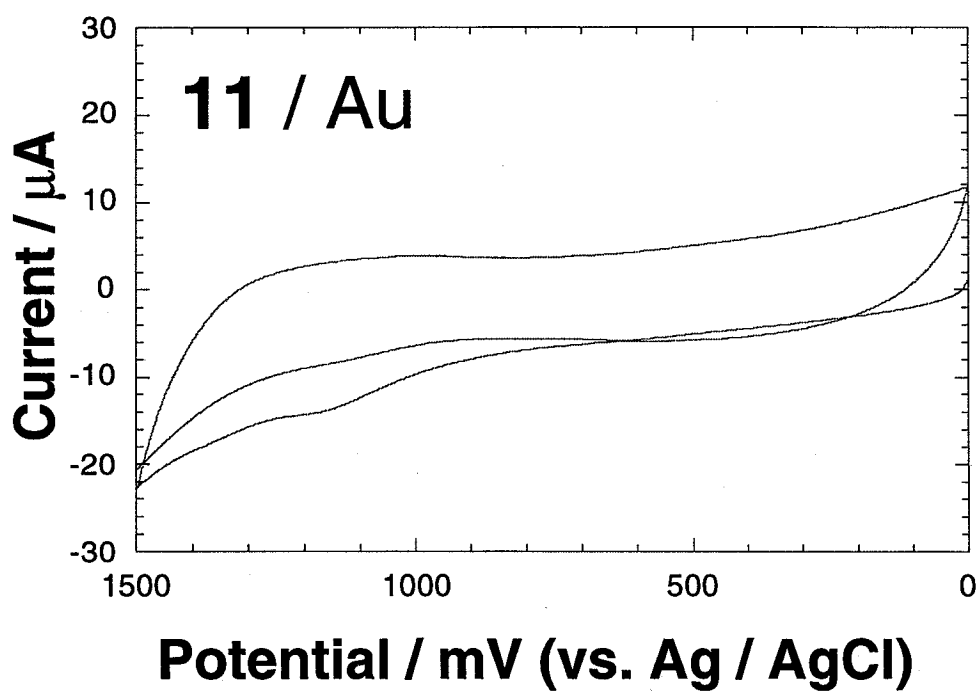
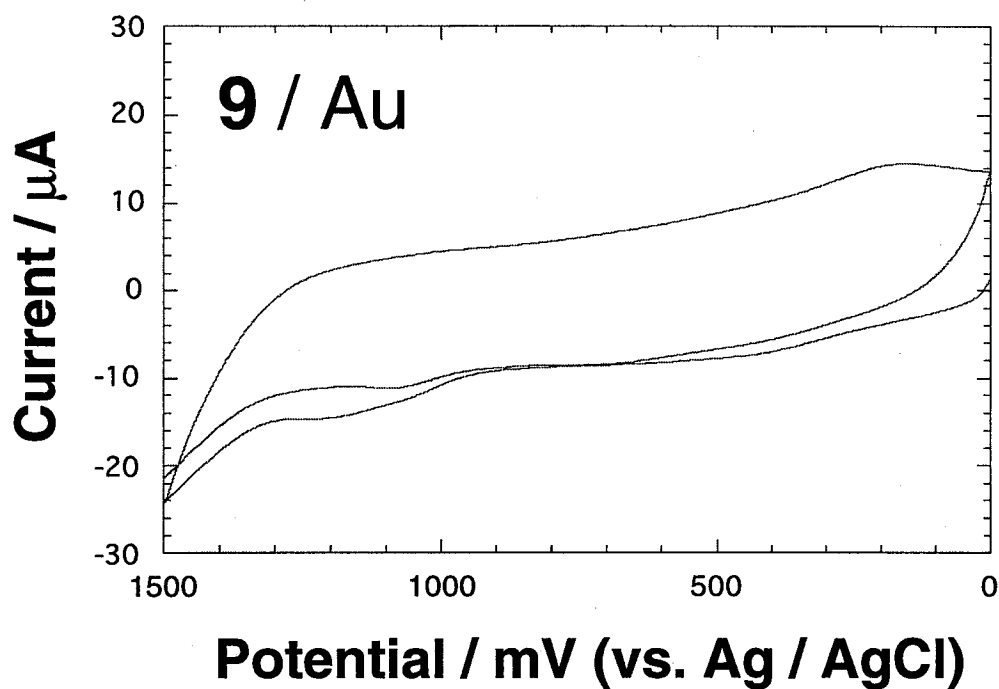
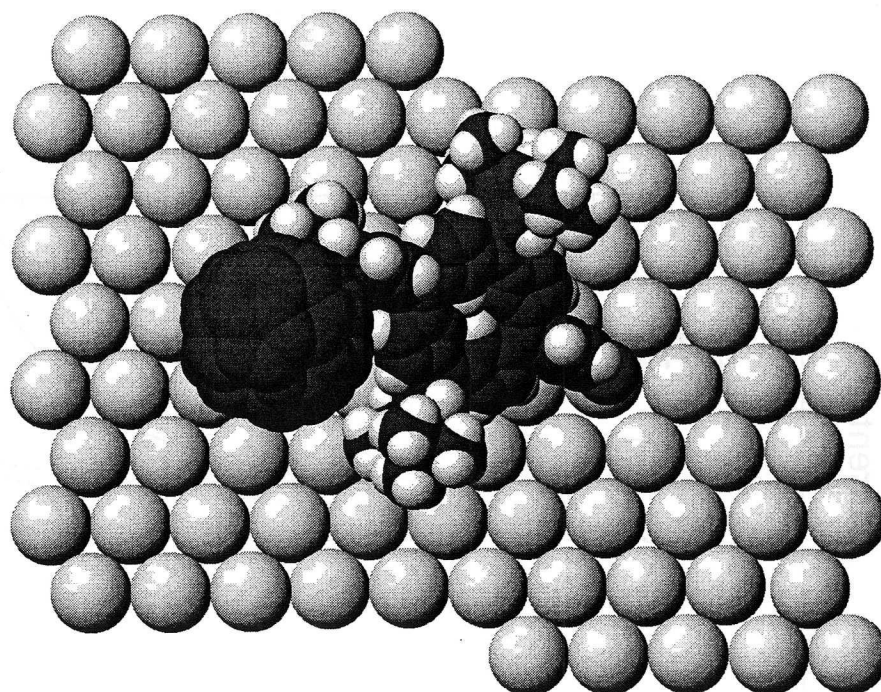


Figure 18 Reflective Absorption Spectra of **11** / Au



Electrolyte : 0.1M  $n\text{-Bu}_4\text{NPF}_6$  in  $\text{CH}_2\text{Cl}_2$ , reference electrode : Ag / AgCl,  
counter electrode : Pt wire, scan rate : 500mV / sec

Figure 19 Cyclic Voltammetry



$310.6 \text{ \AA}^2 / \text{molecule}$

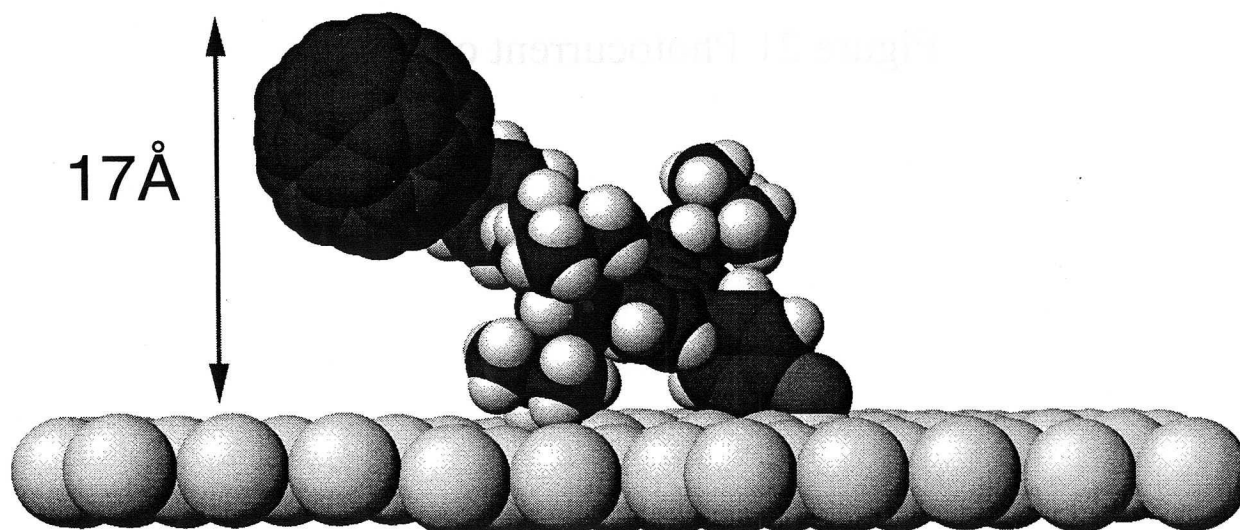
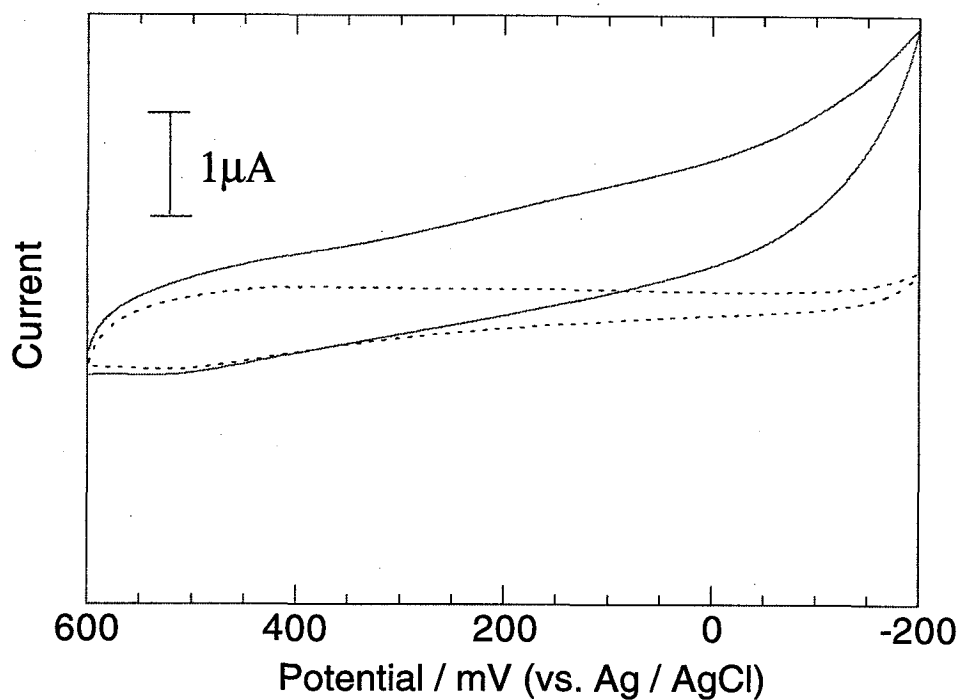
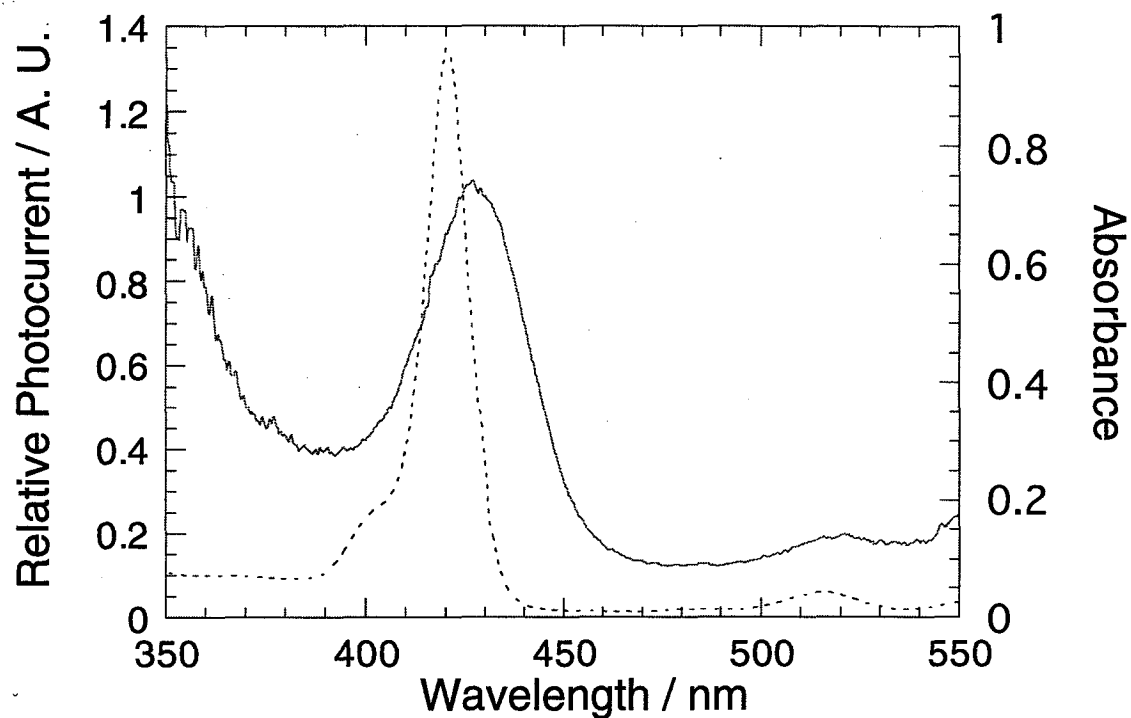


Figure 20 Molecular Mechanics Calculations of **9** / Au



Working Electrode : Modified Au Electrode, Reference Electrode : Ag / AgCl, Counter Electrode : Pt, Supporting Electrolyte: 0.1M Na<sub>2</sub>SO<sub>4</sub>aq, Electron Carrier: 5mM Methylviologen, Light : 150W Xe Lamp, Scan Rate : 500mV / sec, real line : light, dashed line : dark

Figure 21 Photocurrent of **9** / Au



Working Electrode : Modified Au Electrode, Reference Electrode : Ag / AgCl, Counter Electrode : Pt, Supporting Electrolyte: 0.1M Na<sub>2</sub>SO<sub>4</sub>aq, Electron Carrier: 5mM Methylviologen, Light : 300W Xe Lamp, Observed Potential : 0mV, real line : photocurrent of 9 / Au, dashed line : electronic absorption spectrum of 9 in THF

Figure 22 Action Spectrum of 9 / Au

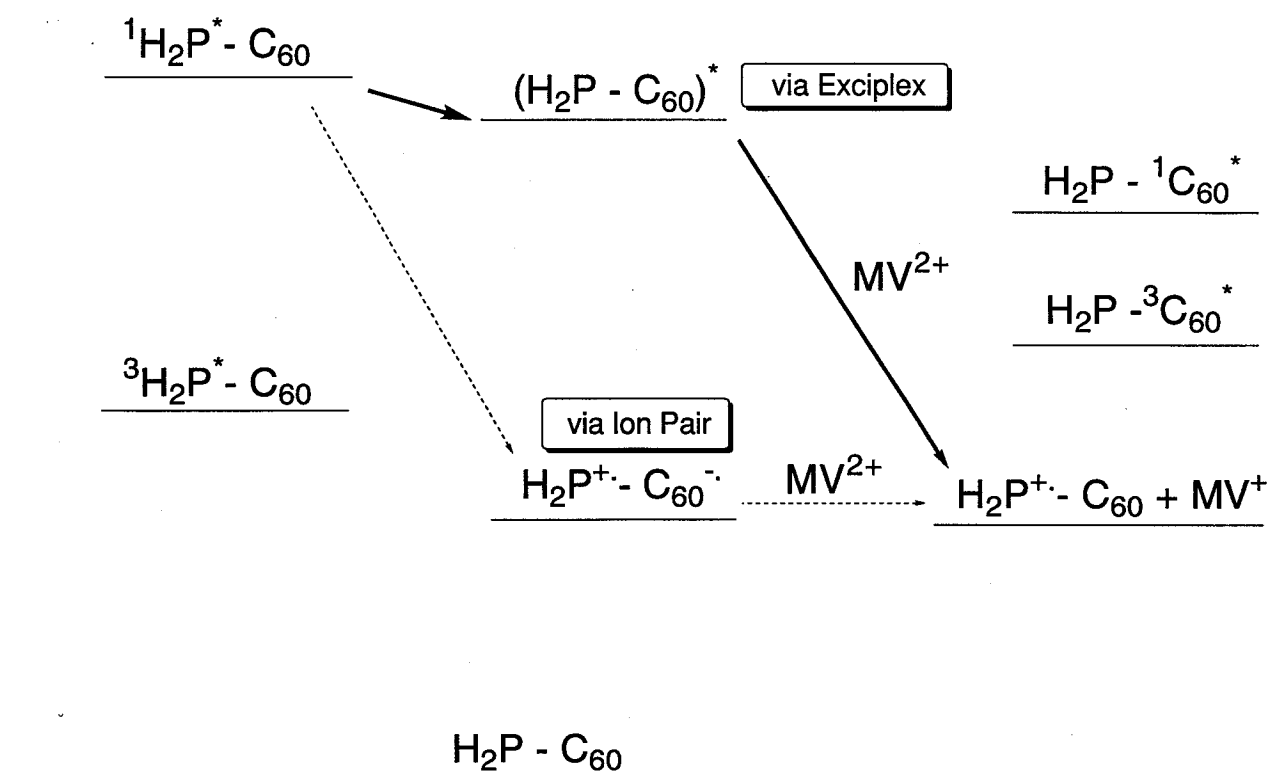


Figure 23 Possible Mechanism of Photocurrent Generation

# Conclusion

The current interest in the field of artificial photosynthesis using organic molecules is derived from the research of photosynthetic model compounds and the techniques of assembling molecules. In this research, the author have investigated large and functional molecular assembly and their function as a assemblies.

In Chapter 1, Porphyrin dimers bering disulfide bond were designed and synthesized. Porphyrin molecular assemblies on gold were prepared. Photocurrent was produced using one-molecular system.

In Chapter 2, Porphyrin-linked fullerene molecules were designed and synthesized. Porphyrin-linked fullerene molecular assemblies were prepared. Formed two-molecular system was able to produce photocurrent as  $\mu\text{A}$  level. These photocurrent generation was much effected by structure of molecular assembly and photophysical properties of donor-acceptor molecules.

The author believes that these new findings provide useful information to open the next door in the filed of artificial photosynthesis.

# Publications

## List of Publications

- 1) Preparation of Molecular Assemblies of Porphyrin-Linked Alkanethiol on Gold Surface and Their Redox Properties.  
T. Akiyama, H. Imahori, and Y. Sakata, *Chem. Lett.*, **1994**, 1447-1450.
- 2) Synthesis and Self-Assembly of Porphyrin-linked Fullerene on Gold Surface Using S-Au Linkage.  
T. Akiyama, H. Imahori, A. Ajawakom, and Y. Sakata, *Chem. Lett.*, **1996**, 907-908.
- 3) Large Photocurrent in Modified Gold Electrode with Self-Assembled Porphyrin-Linked Fullerene.  
T. Akiyama, H. Imahori, A. Ajawakom, and Y. Sakata, *in preparation*.

## Other Publications

- 1) Synthesis and Photophysical Property of Porphyrin-linked Fullerene.  
H. Imahori, M. Aoki, T. Akiyama, S. Taniguchi, T. Okada, and Y. Sakata. *Chem. Lett.*, **1995**, 265-266.
- 2) Linkage and Solvent Dependence of Photoinduced Electron Transfer in Zincporphyrin-C<sub>60</sub> Dyads.  
H. Imahori, K. Hagiwara, M. Aoki, T. Akiyama, S. Taniguchi, T. Okada, M. Shirakawa, and Y. Sakata, *J. Am. Chem. Soc.*, 1996, **118**, 11771-11782.
- 3) The Small Reorganization Energy of C<sub>60</sub> in Electron Transfer.  
H. Imahori, K. Hagiwara, T. Akiyama, M. Aoki, S. Taniguchi, T. Okada, M. Shirakawa, and Y. Sakata, *Chem. Phys. Lett.*, *in press*.
- 4) Synthesis and Photophysical Properties of Porphyrin-C<sub>60</sub> Dyads.  
H. Imahori, M. Aoki, T. Akiyama, Y. Sakata, K. Hagiwara, and T. Okada, Recent Advances in the Chemistry and Physics of Fullerenes, Vol. 3, 332-341.
- 5) Control of Electron Transfer and Its Utilization.  
Y. Sakata, H. Imahori, H. Tsue, S. Higashida, T. Akiyama, E. Yoshizawa, M. Aoki, K. Yamada, K. Hagiwara, S. Taniguchi, and T. Okada, *Pure & Appl. Chem.*, *in press*.