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TSUYOSHI AKIYAMA

Department of Applied Fine Chemistry
Faculty of Engineering
Osaka University
1997

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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)

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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 syste, which mimics photosynthetic electron transfer.

The author wishes to express his sincere gratitude to Propfessor 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 advise, stimulating discussions, and hearty encouragement.

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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 heaty encouragement.

Osaka, Japan

January, 1997

Tsuyoshi Akiyama

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General Introduction

Recently much utilization of solar energy has been studied extensively releavant to enviromental 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 an 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 chromophores are 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 govering rates of ET reactions including driving forces, distances and orientations, the nature of intervening medium, and solvent. Some of these well-defied models, such as triad, tetrad, and pentad have displayed long-lived charge separated states with high quantum yield. Although these sucess has enabled us to control reaction mode as well as efficiency of CS in donor-acceptor linked molecules. There is sitll fundamental problem to be solved for for application of these molecules in light energy conversion system: How canwe orient and arrange these molecules unidirectionally? A variety of method have been utilized, to assemble fundamental molecules such as, langmuir-blodgett films, bilayers, polymers, miscells, and vesicles and so on. However, these methods have disadvantage in stability and regularity. I have chosen self-assembled monolayer techniques was introduced during the last decade. It eneble the molecules of interest to be bound chemically on the suraface like matals, smiconductors, and insulates in a highly organized and less defective manner. Especially, sulfur compounds (thiols, disulfides, and sulfides) bind to gold tightly form highly-oriented and stable monolayers. There have been manu reports about the modified electrode with redox active molecules using self-assembling method. Therefore, this film seems tobe the most promissing 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 dioxgen. 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 contorolling factors to obtain the SAM in highly regular manner. Thus, Van der Waals interaction between alkyl chains as well as π-π 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 cartenoids 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 permation chromatography with CHCl3 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 CH_2Cl_2 solution of **4** or **5** for 24hr, wased well with enough amount of CH_2Cl_2 and dried with a stream of N_2 (Fig. 4). Electrochemical cell for all measurment 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 immmobilized on the electrode surface. It should be noted here that relative intensities of alfa 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 siginificantly 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 $S(2p_{3/2})$ energies were observed for 4 / Au and 5 / Au, respectively. These values (**4** / Au : 162.1 eV, **5** / Au : 162.2 eV) are in gold agreement with the reported values of $S(2p_{3/2})$ (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 voltamograms 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 appearant 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 CH_2Cl_2 (803 mV, 1124 mV). It should be noted here that the peak splitting between the forground and back waves are unusually large. It may be ascribed to the relating slow ET between the electrode and the porphyrin or counter anion for the porphyrin. Number of the adsorbed molecules for **5** / Au was estimated to be 5.9 x 10-11 mol / cm^2. 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 clealy seen at negative potentials at around -200 mV (vs. Ag / AgCl) in the presence of methylviologen. In contrast, no appearant 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 resonably 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 differenece for peak position of Soret and Q bands may results from differenece between the enviroments in the porphyrin on the surface and in solution. Possible mechanism is shown in Figure 10. After excitation of the porphyrin, excited siglet and triplet states of the porphyin are produced. Intermolecular ET from the excited states to MV^{2+} 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 (CH_2Cl_2). The second band was collected and concentrated under reduced pressure, and the residue was recrystallized from CH_2Cl_2 / Hex to give porphyrin **1** as purple cryctal (0.48g, 0.67mmol, 1.1%).

1: purple crystal, mp >300 °C. ^{1}H-NMR ($CDCl_3$) δ = 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 NaHCO3aq. The organic layer was concentrated under reduced pressure, and the residue was purified with flush column chromatography (CH_2Cl_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}H-NMR ($CDCl_3$) δ = 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-methylmorphorin (40.0ml, 0.365mmol) was added to the solution with dropwise, and stirred for 1hr. Porphyrin **2** (250mg, 0.372mmol) and N-methylmorphorin (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 CH_2Cl_2 and neutralized with $NaHCO_3$aq. The oraganic 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 recrystalized from CH_2Cl_2 / hex to give porphyrin **4** as dark red powder (170mg, 0.098mmol, 52.7%).

4: dark red powder, mp >300 °C. ^{1}H-NMR (CDCl3) 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 C116H112N10S2O2 : 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_2Cl_2 (20ml). MeOH saturated Zn $(OAc)_2$ (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_2Cl_2). Pink colored band was collected and evaporated. The residue was recrystalized from CH_2Cl_2 / 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. Mujsce, *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 Functioal 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 reratively 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 in slower compared with the decay of the exited states of the porphyrin. To generate photocurrent more efficiently. The aim of this study is construction of mutistep electron transfer system which mimic photosynthesis. Such multistep electron transfer reactions could produce charge separated states with high quantum yield. To control intermolecular ET, sutable donor and acceptor should be chosen linked together in moderate manner. Porphyrins also employed as a light harvesting donor and fullerene are as an acceptor. There are some advantage for usage of fullerenes as an acceptor : i) fullerenes are stable and durable under severe conditions. ii) fullerenes are good electron acceptor. iii) fullernes accelerate CS and retard back ET. These unique characteristics provide a new opptunity 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 contaning methylthio group was designed (Fig. 11). Bearing these in mind, such molecules and sequential vectrial ET relay occurs after the excitation of the chromophores. Thus, initial efficient CS within the porphyrin-linked fullerenes followed by intermolecule 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 $Zn(OAc)_2$ in $CHCl_3$ gave a mixtures of several porphyrins. The desired product was separated by flash column chromatography (Fujisilisia BW300 / C_6H_6) and hydrolized to give **8**. Porphyrin-linked C_{60} **9** was obtained by 1,3-dipolar cycloaddition using **8**, N-methylglycine, and 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 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 CH_2Cl_2 solution of **9-13** for 4days to equiblirate adsorprion. These samples of these molecules on the surface were washed well with enough amount of CH_2Cl_2 and dried with a stream of N_2. Electrochemical measurement was performed on Bioanalytical Systems, Inc. CV-50W and Huso Electro Chemical System, Inc. HECS 315B, HECS 321B, and HECS 311B. Monochrometer 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 measurment was shown in Fig. 5. X-ray photoelectron spectroscopy was performed on VG SCIENTIFIC, INC. μLab mark III with MgKa X-ray (1253.6 eV, 8kV, 16mA). Molecular mechanics calclulation 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_{60}.

Redox potentials of **9-13** were measured with cyclicvoltametly in CH_2Cl_2. Redox potentials of **9** (1.24, 0.90, -0.67, -1.06, -1.26 V vs. Ag / AgCl) in CH_2Cl_2 using 0.1 mol dm^{-3} Bu_4NPF_6 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 these 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 singllephoton 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 insturumentation, which are consisitent 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 aroud 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 in ascribed to the zinc porphyrin cation and 920nm band in to $C60^{\cdot-}$. 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_3-Au linkages.

Mass spectroscopy with time of flight method

Ga^+ ionization TOF mass

Fig. 16 show Ga^+ 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_3-Au linkages as biproduct were detected. It may S-Au linkage is too strong to cleave by Ga^+ ionization.

Laser inonization TOF mass

Fig. 17 show Laser inonization 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^{-1} was assigned to aromatic C-H vibration, and the peaks near 2970, 2905, 2850cm^{-1} 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_{60} moity were detected for **9** / Au because of extensibe cleavage of S-Au bond. Numbers of adsorbed molecules in **9**/ Au and **11** / Au were estimated to be 1.6 x 10-11 mol / cm^2 and 0.6 x 10^{-11} mol / cm^2. These values are much smaller compared with alkanethiol / Au systems.

Ellipsometry

The results of ellipsometry measurements showed the thickness of **9** / Au was 13.2Å. 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 hight of the molecules is17Å, and one molecule occupies 310.6Å in area. The height is in godd 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_2SO_4 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 apperent 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^{2+}. 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_{60} 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 (H2P$^{\cdot+}$-C60-MV^{+}). Maginitude of the photocurrent for **9** / Au system increases of MV^{2+}, showing that rate-determing 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 apperarant photocurrent was observed in the case of **10** / Au. Possible explanation is that the rate for intermolecular ET from the C60$^{\cdot-}$ in charge-separated state (ZnP$^{\cdot+}$-C60$^{\cdot-}$ because ZnP$^{\cdot+}$-C60$^{\cdot-}$+MV^{2+} and ZnP$^{\cdot+}$-C60+MV^{+} are similar in energy. The fact that BV^{2+} instead of MV^{2+} increases the photocurrent is consistent with this reaction machenism. Possible mechanism is shown in Figure 23.

2.4 Conclusion

Porphyrin-linked fullerenes bearing methylthio group were synthesized.

Porphyrin-linked fullerenes sturucture were immmobilized 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 NaHCO3aq. The organic layer was separated and dried over Na2SO4. 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}H-NMR ($CDCl_3$) δ = 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) benzylalchol.

To a solution of methyl-4-(5,5-dimethyl-1,3-dioxan-2-yl)-benzoate (48.3g, 0.19mol) in THF (400ml) was added $LiAlH_4$ (12.07g, 0.32mol) at 0°C. The mixture was stirred for 12h. The reaction was quenched with EtOAc and H2O at 0oC, and 1M HClaq, it was extracted with EtOAc. The organic layer was washed with water, and dried over Na_2SO_4. The solvent was removed under reduced pressure to give 4-(5,5-dimethyl-1,3-dioxan-2-yl) benzylalchol. as oil (41.7g, 0.188mol, 97% yield).

4-(5,5-dimethyl-1,3-dioxan-2-yl) benzylalchol: Colorless oil. ^{1}H-NMR ($CDCl_3$) δ = 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) benzylalchol (41.7g, 0.188mol) in CH_2Cl_2 (200ml) was added PCC (60.6g, 0.282mol) dropwise, and CH_3CO_2Na (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}H-NMR ($CDCl_3$) δ = 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 N_2 for 15min and CF_3COOH (0.08ml, 1mmol) was added and stirred for 15min. To the mixture was poured $CHCl_3$ (1000ml) and washed with 0.1M NaOHaq, H_20. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified flush column chromatography ($CHCl_3$). The second band was collected and evaporated to give **6** (18.41g, 55.1mmol, 55% yield).

6: pink crystal, mp >300 °C. ^{1}H-NMR ($CDCl_3$) $\delta = 7.91$ (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 CH_3CN (700ml). The mixture was stirred overnight. To the solution was added Chroranil (3g) stirred for additional 5h. The mixture was washed with $NaHCO_3$aq and NaClaq. The organic layer was separated and dried over Na_2SO_4. After filtration, to the mixture a saturated $Zn(OAc)_2$ MeOH solution (50ml) was added. The mizture 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 °C. ^{1}H-NMR ($CDCl_3$) $\delta = 9.00 - 8.90$ (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 $(M+1)^+$. Calcd. for C67H72N4O2SZn : 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), CF_3COOH (5ml), CH_3COOH (10ml) and 5% H_2SO_4 (2.5ml) were mixed in the flask. The reaction mixture was heated to 100°C and stirred for 2h. The solution was diluted with water and extracted with $CHCl_3$. The organic layer was washed with $NaHCO_3$aq and dried over Na_2SO_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. ^{1}H-NMR ($CDCl_3$) 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 $(M+1)^+$. Calcd. for C62H64N4OS : 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_{60} (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. ^{1}H-NMR ($CDCl_3$) 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). ^{13}C-NMR (67.5 MHz, CDCl3) 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 $(M+1)^+$. UV-Vis (THF) λ max 420, 515, 552, 591, 649 nm. Calcd. for C124H69N5S : 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, 7.82umol) was dissolved in $CHCl_3$ (20ml). $Zn(OAc)_2$ 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_2SO_4 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 benzene / MeOH to give **10** as brown powder (12.3mg, 7.13umol, 91% yield).

10: brown powder, mp >300 °C. ^{1}H-NMR ($CDCl_3$) 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 $(M+1)^+$. Calcd. for C125H69N5SZn : 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 pyrolle (2.51g, 3.75mmol, 2.6ml) were dissolved in dry $CHCl_3$ (900ml). The mixture was degassed with N_2. Then, $BF_3(OEt)_2$ (3.2ml) was added to the solution and stirred for 2hr with N_2 atomosphere. 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, $CHCl_3$, benzen / hexane = 1 / 1). The second band was collected and evaporated. The residue was recrystallized from benzen / CH_3CN to give **11** as dark red powder (0.12g, 0.12mmol, 13% yield).

11: reddish powder, mp >300 °C. ^{1}H-NMR ($CDCl_3$) 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 $(M+1)^+$. Calcd. for C69H80N4S :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 $CHCl_3$ (100ml) was added a saturated $Zn(OAc)_2$ in MeOH solution (10ml). The mixture was refluxed for 10min. After cooling, the organic layer was washed with water, and the $CHCl_3$ layer was dried over Na_2SO_4. 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. ^{1}H-NMR ($CDCl_3$) 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 $(M+1)^+$. Calcd. for C69H78N4SZn :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 Soci ety of Japan, Tokyo, March 1994, Abstr. No. 1L526.

13) S. Yamada, H. Kohrogi, 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

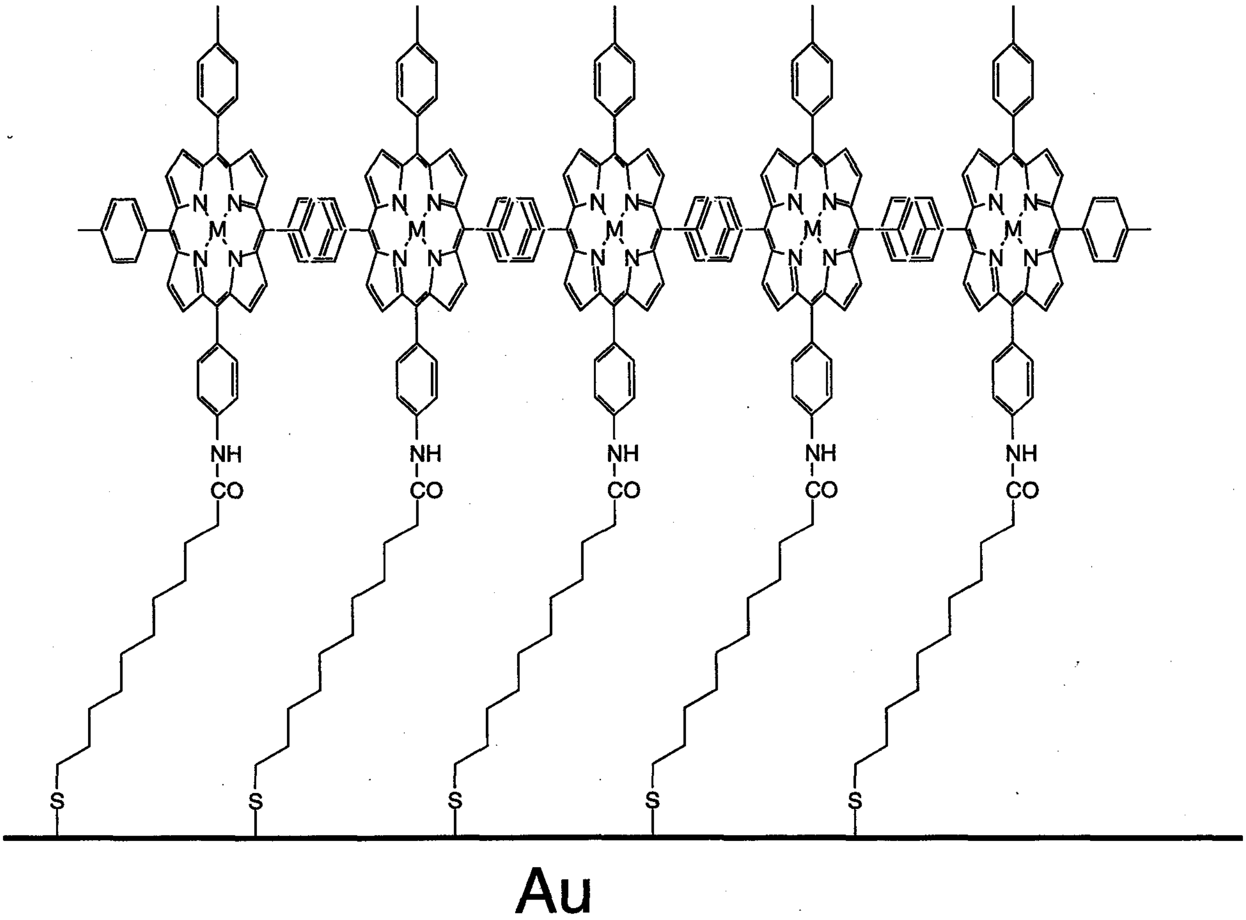


Figure 1 Porphyrin Molecular Assembly

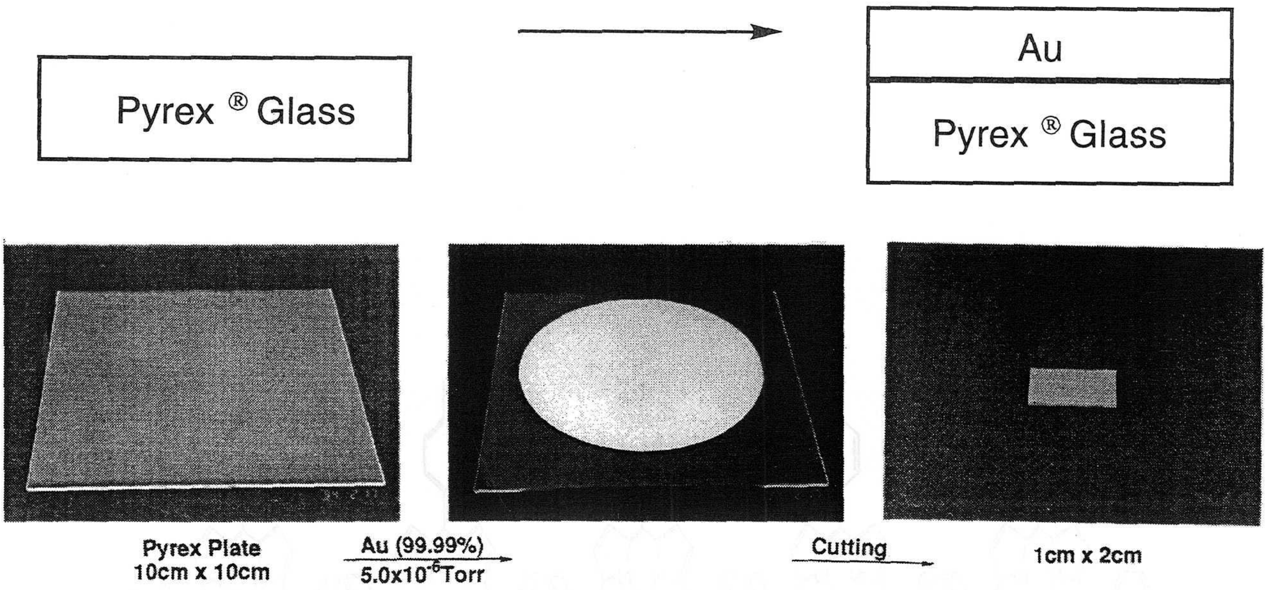
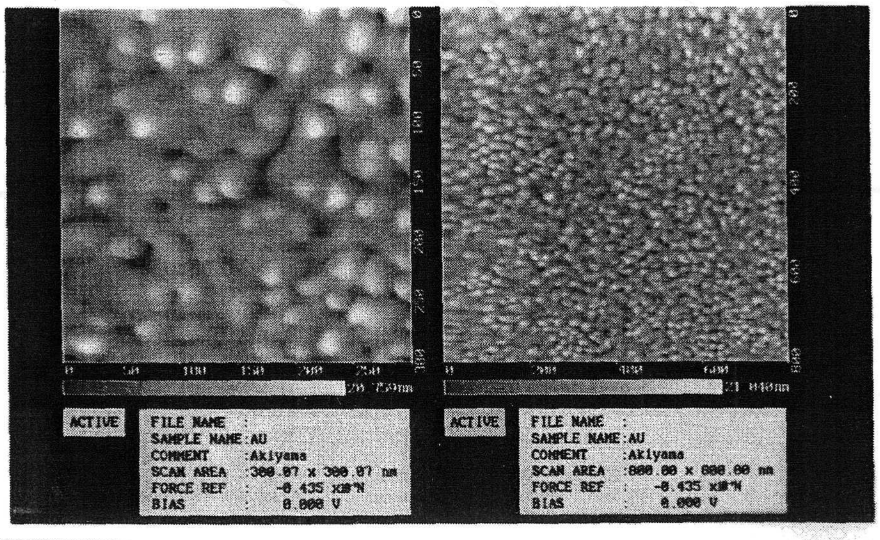


Figure 2 Preparation of Au / Pyrex Electrode

Atomic Force Microscopy



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FORCE REF   :     -0.435 x0*N
BIAS        :      0.000 V
```

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FILE NAME   :
SAMPLE NAME:AU
COMMENT     :Akiyama
SCAN AREA   :800.00 x 800.00 nm
FORCE REF   :     -0.435 x0*N
BIAS        :      0.000 V
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Surface Roughness
Maximum = 200Å
RMS = 27Å

Figure 2-2 AFM Image of Au / Pyrex

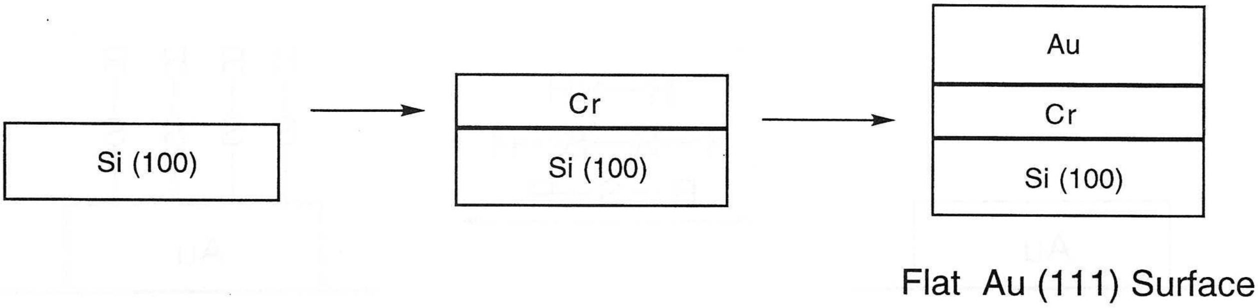


Figure 3 Prepration of Au / Cr / Si (100) Electrode

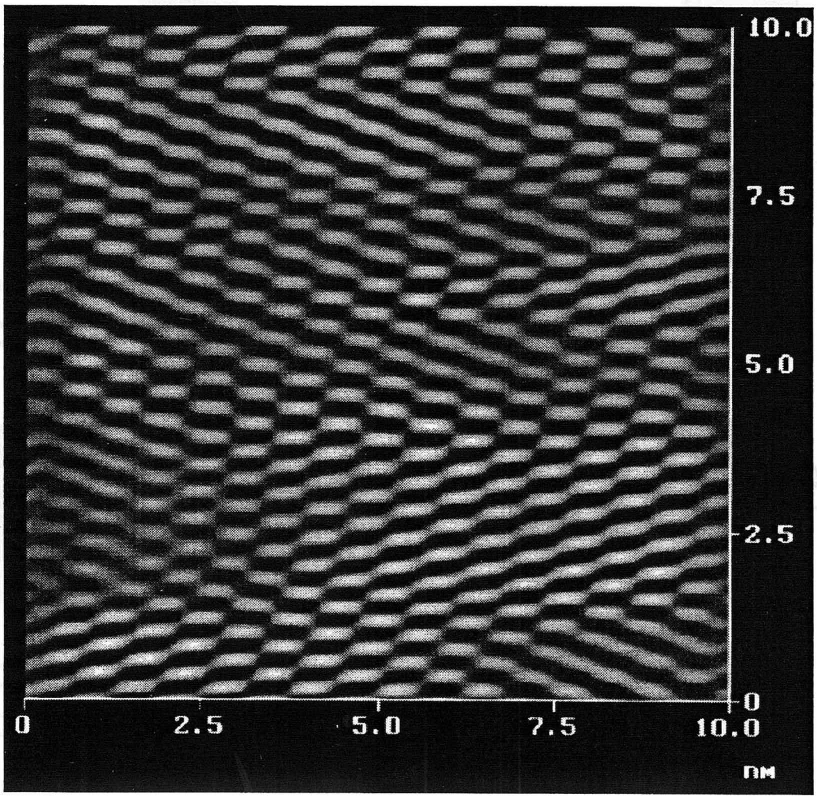
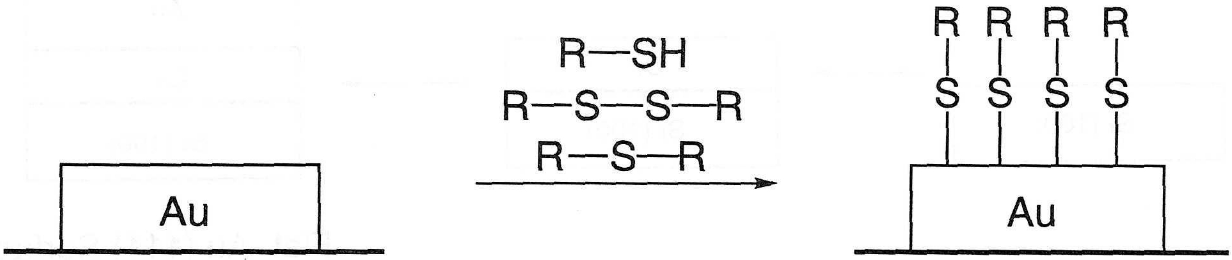


Figure 3-2 AFM Image of Au / Cr / Si (100)



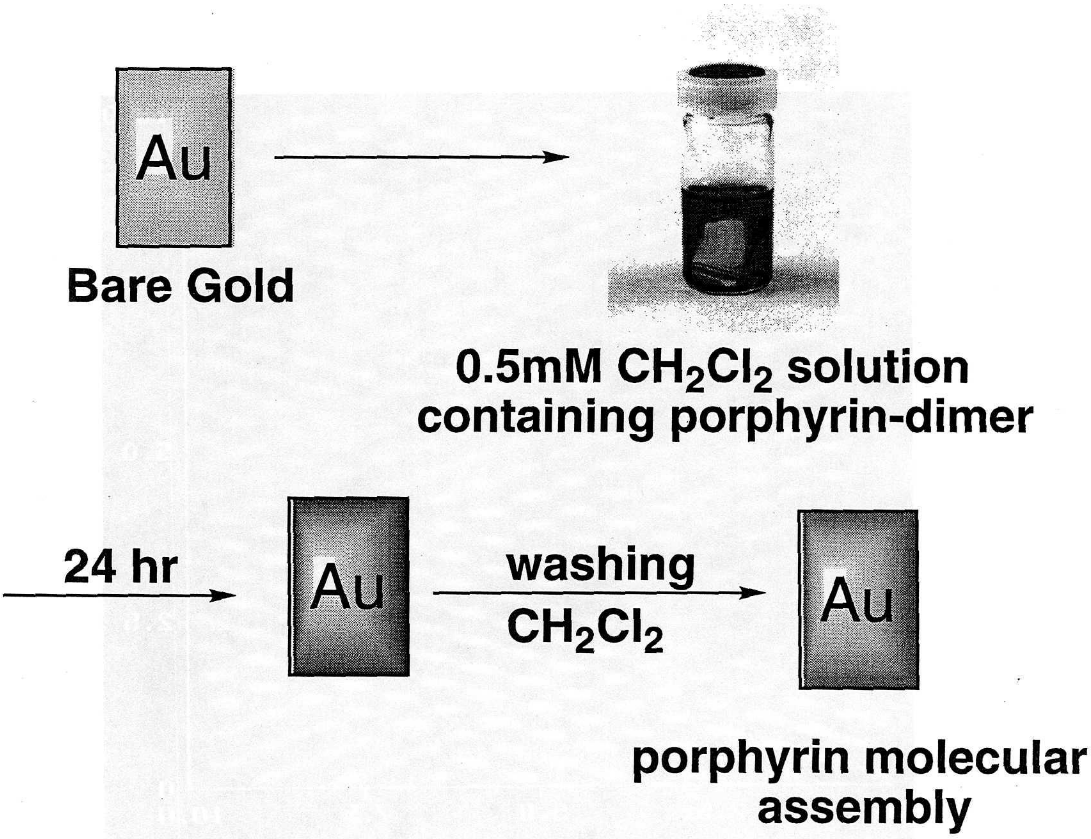


Figure 4 Formation of Self-Assembled Monolayer

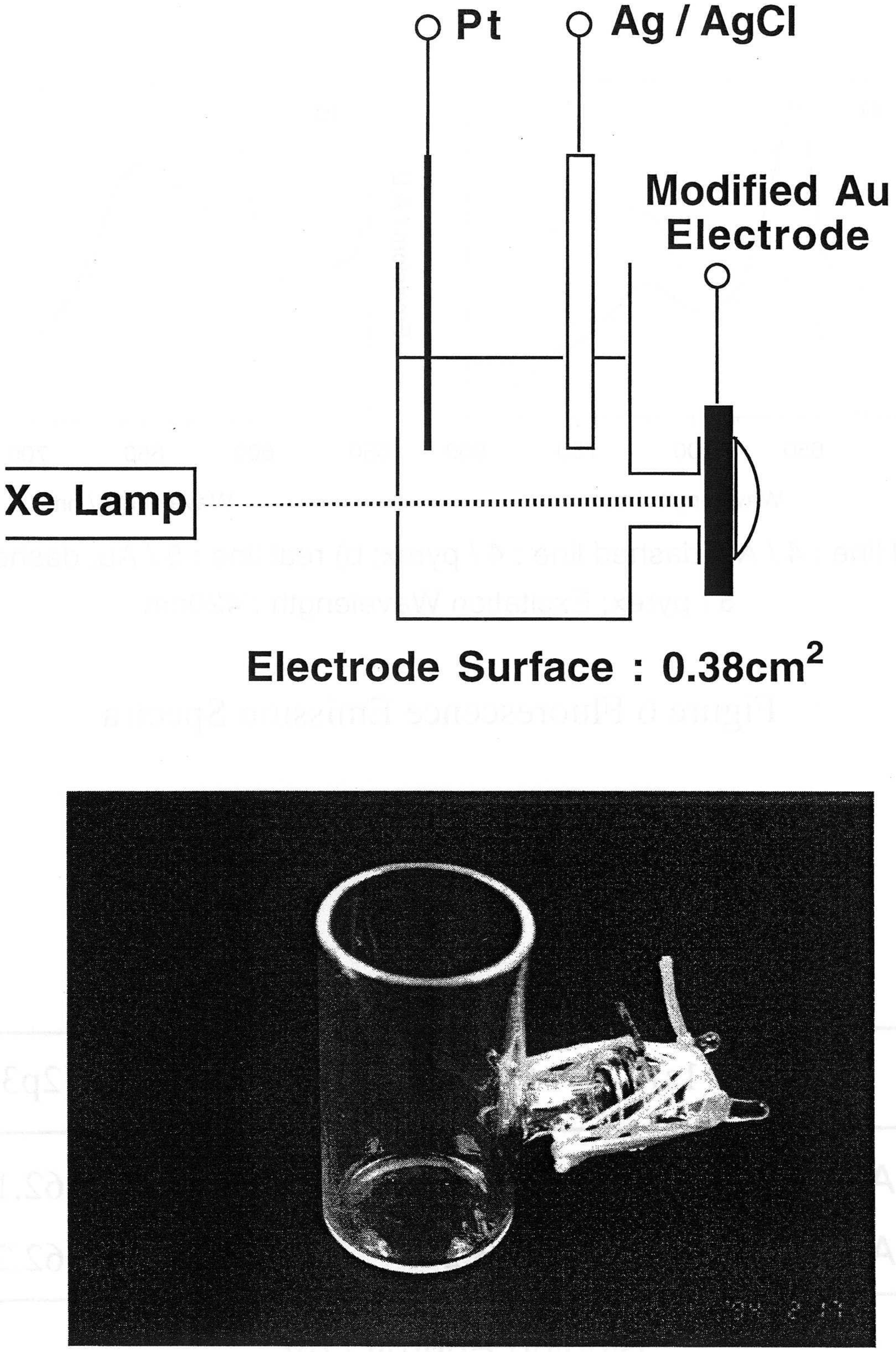
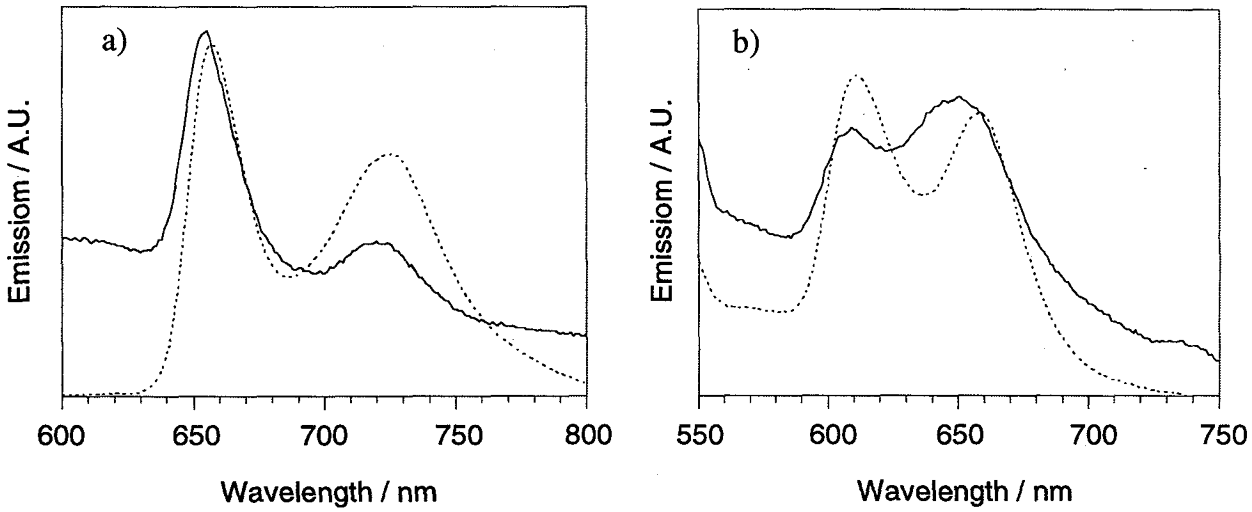


Figure 5 Photoelectrochemical Measurement Cell



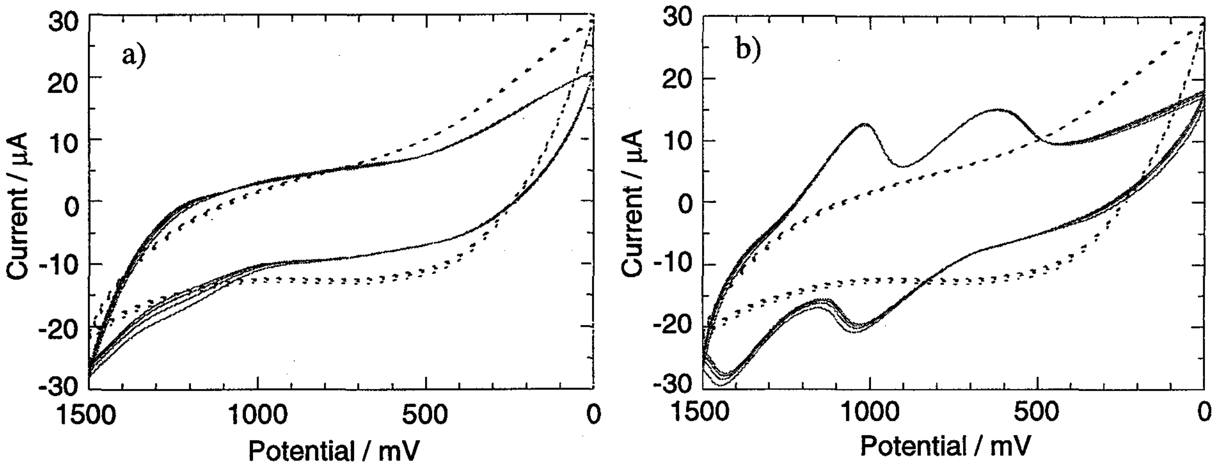
a) real line : **4** / Au, dashed line : **4** / pyrex; b) real line : **5** / Au, dashed line : **5** / pyrex; Excitation Wavelength : 420nm

Figure 6 Fluorescence Emission Spectra

	C (1s)	O (1s)	N (1s)	S (2p3/2)
4 / Au	285.0	533.0	400.0	162.1
5 / Au	285.6	533.2	399.7	162.2

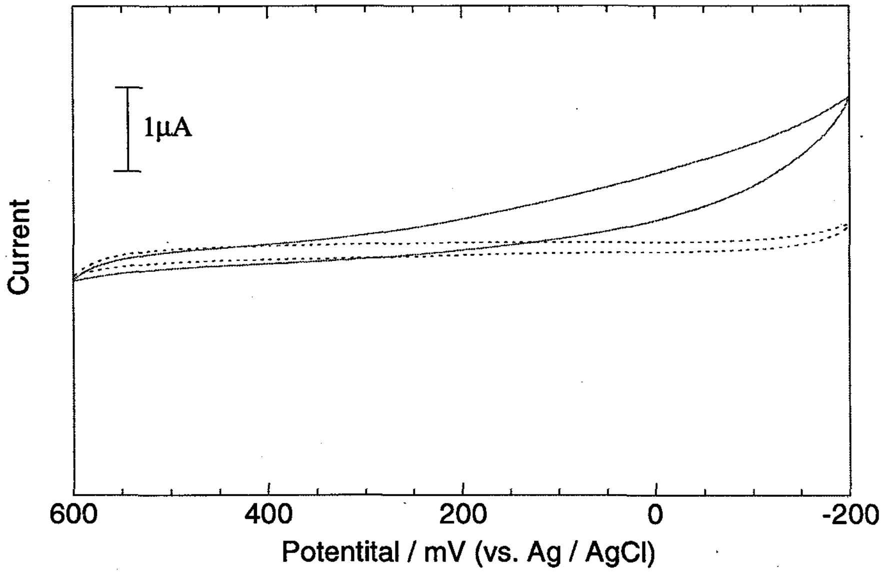
Binding Energy / eV

Table 1 Photoelectron Binding Energy



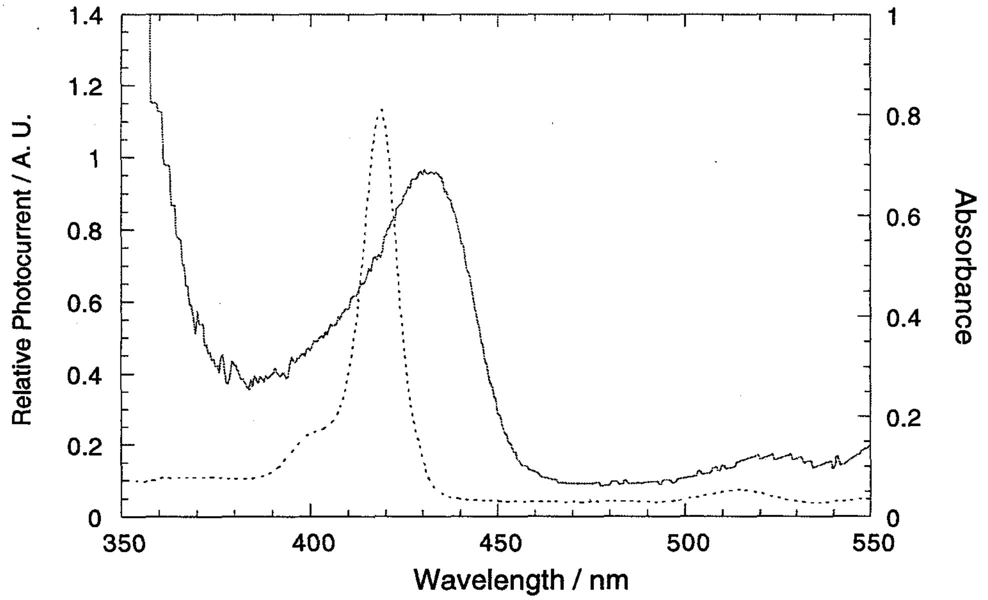
a) real line : **4** / Au, dashed line : bare Au; b) real line : **5** / Au, dashed line : bare Au; Electrolyte : 0.1M n-Bu_4NPF_6 in CH_2Cl_2, referenece electrode : Ag / AgCl, counter electrode : Pt wire, scan rate : 500mV / sec

Figure 7 Cyclic Voltametry



Working Electrode : Modified Au Electrode, Reference Electrode : Ag / AgCl, Counter Electrode : Pt, Supporting Electrolyte: 0.1M Na2SO4aq, 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 Na2SO4aq, Electron Carrier: 5mM Methylviologen, Light : 300W Xe Lamp, Obserbed Potential : 0mV, real line : photocurrent of 4 / Au, dashed line : electronic absorption spectrum of 4 in THF

Figure 9 Action Spectrum of **4** / Au

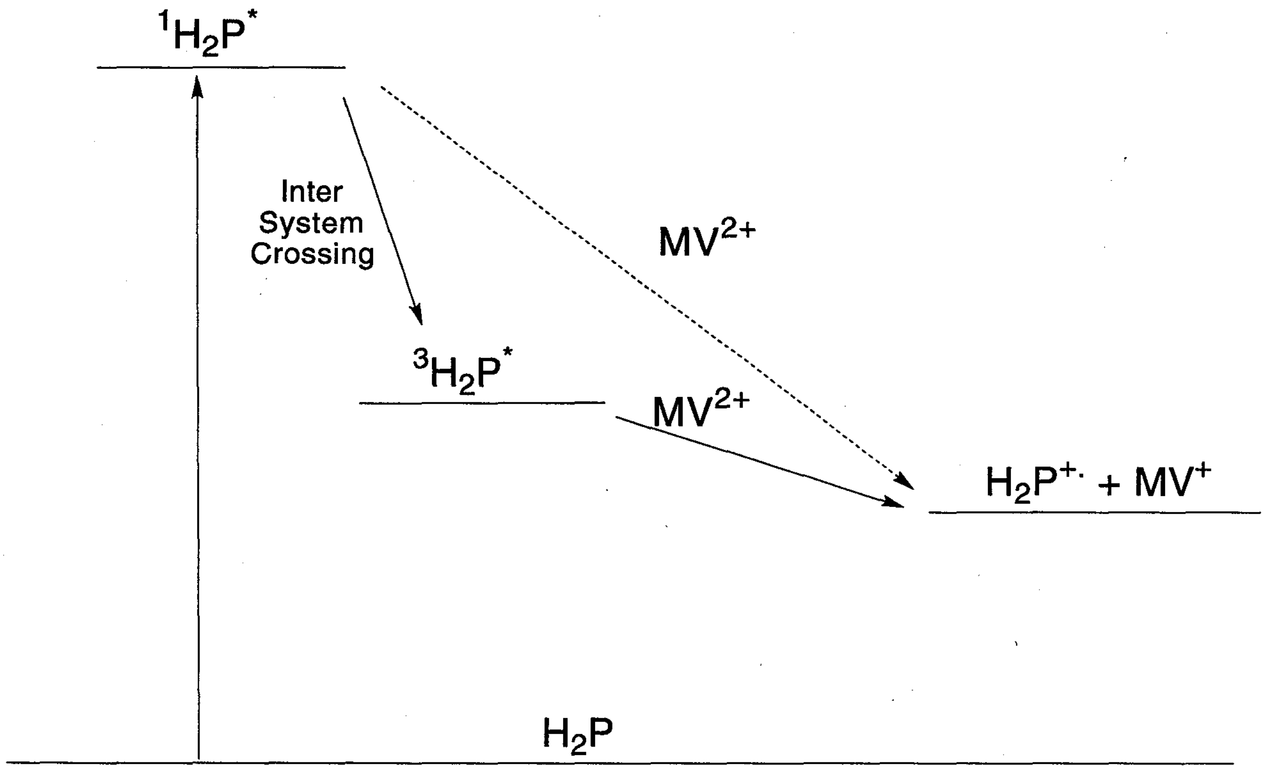
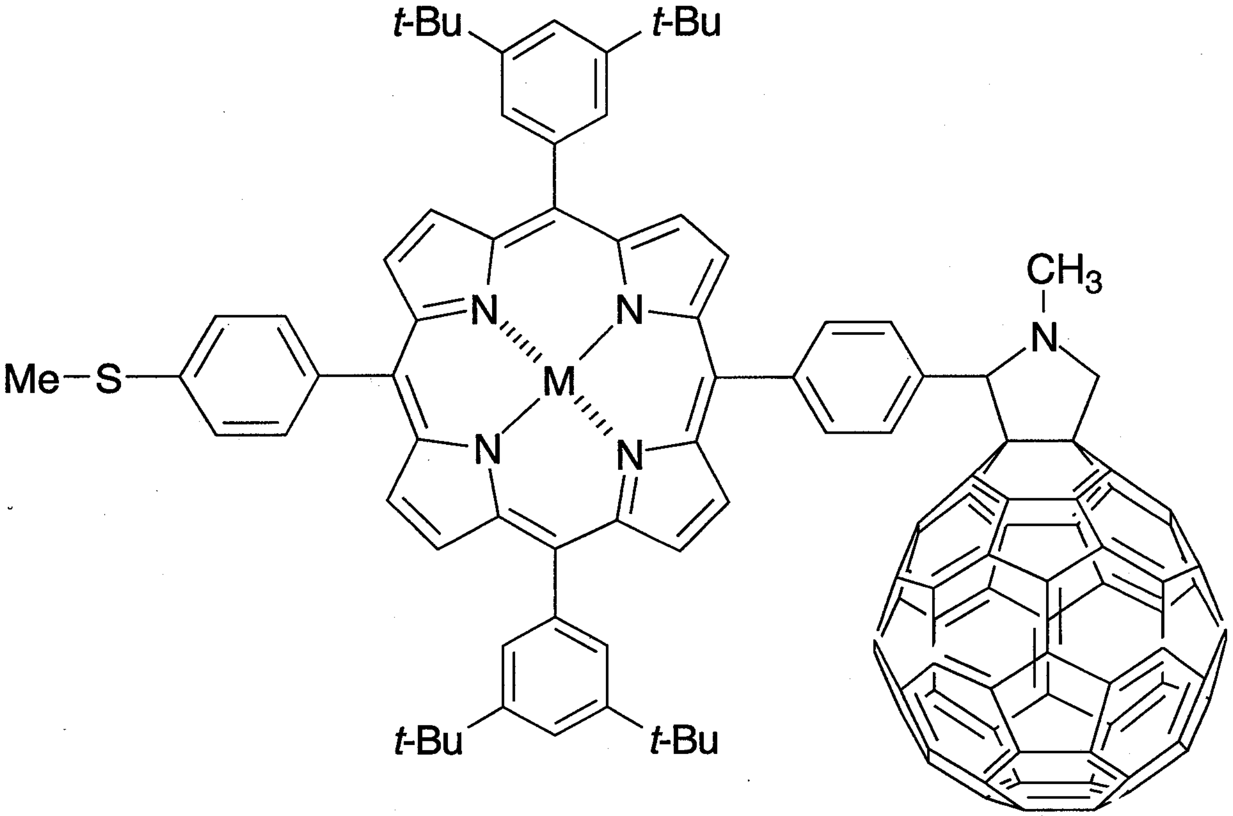


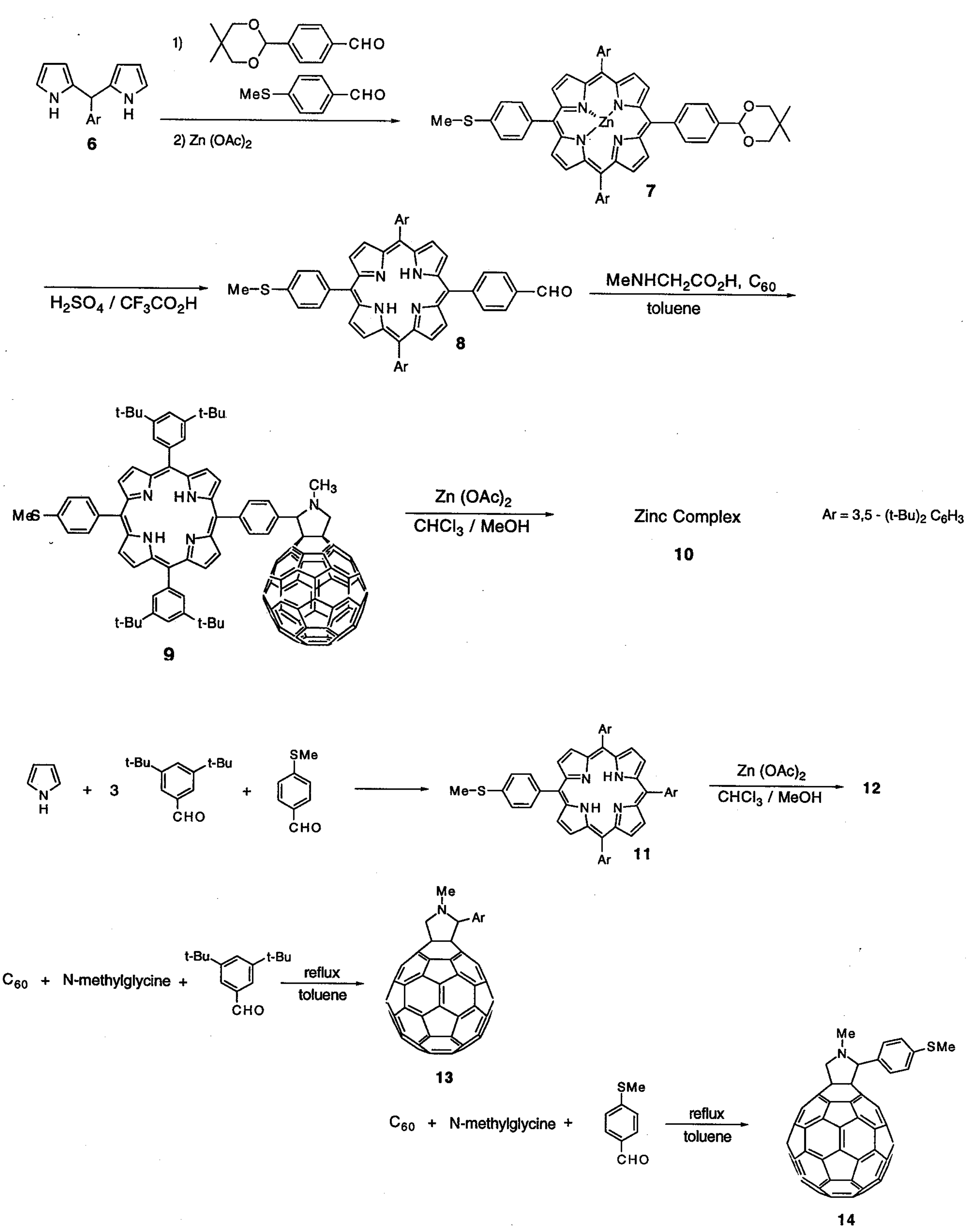
Figure 10 Possible Mechanism of Photocurrent Generation



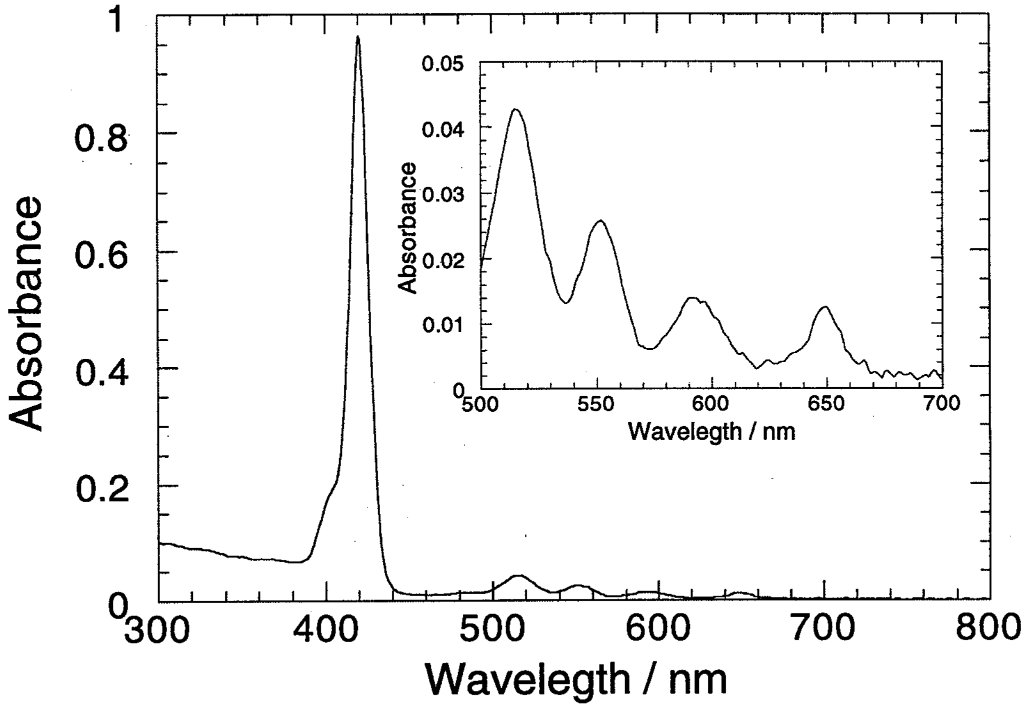
9 (M = 2H)

10 (M = Zn)

Figure 11 Target Compounds

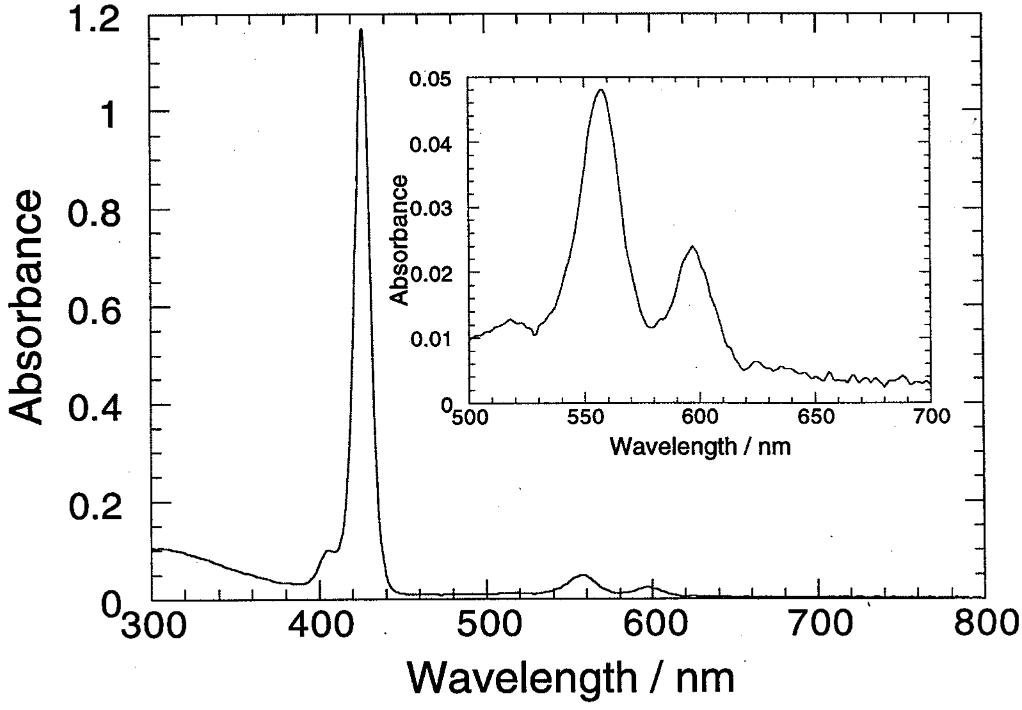


Scheme 2 Synthesis



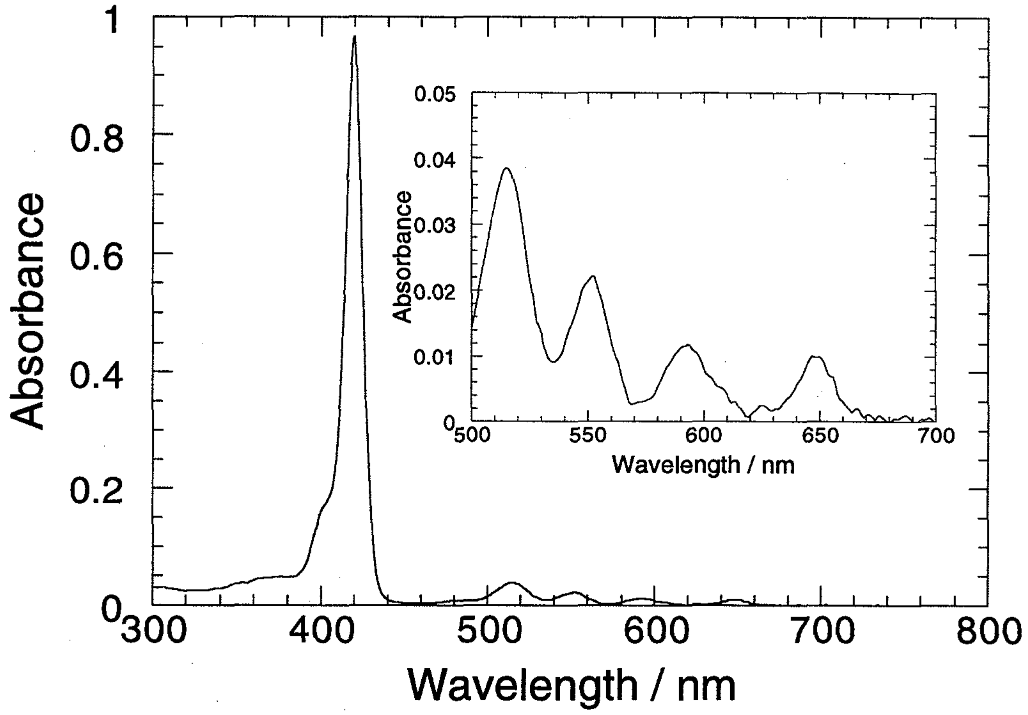
1.81μM in THF

Figure 12 Electronic Absorption Spectra of **9**



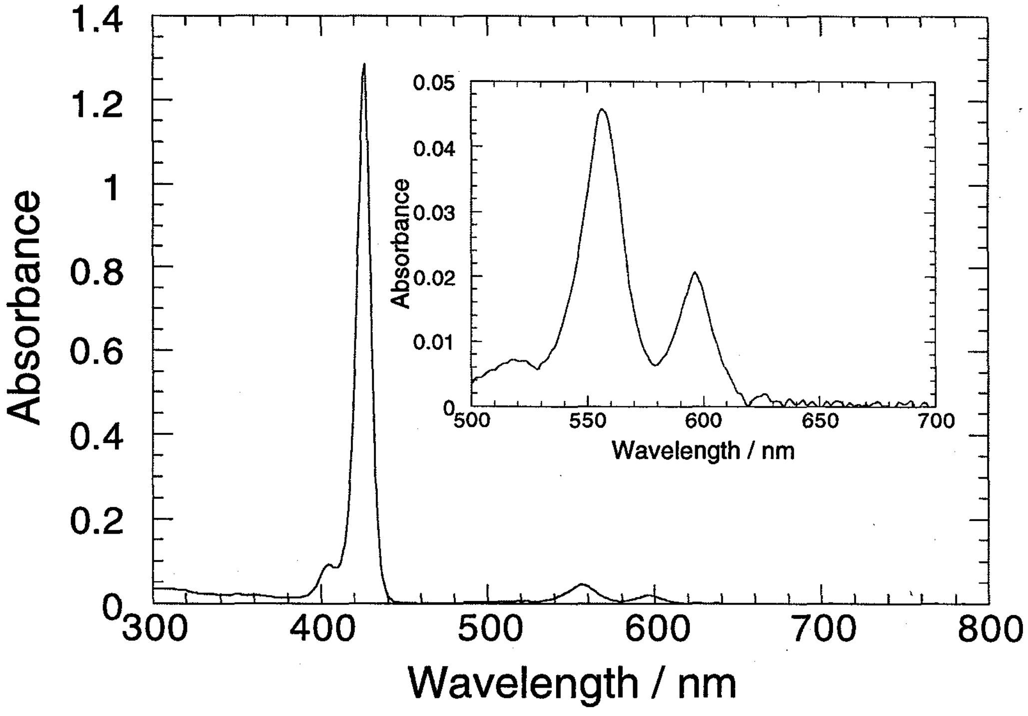
1.81μM in THF

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



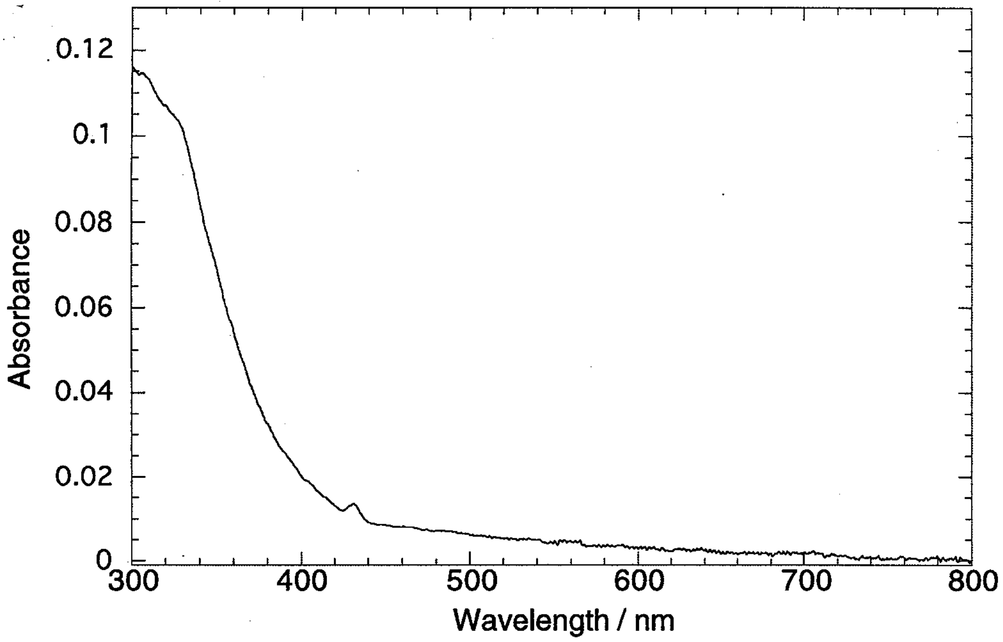
1.81μM in THF

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



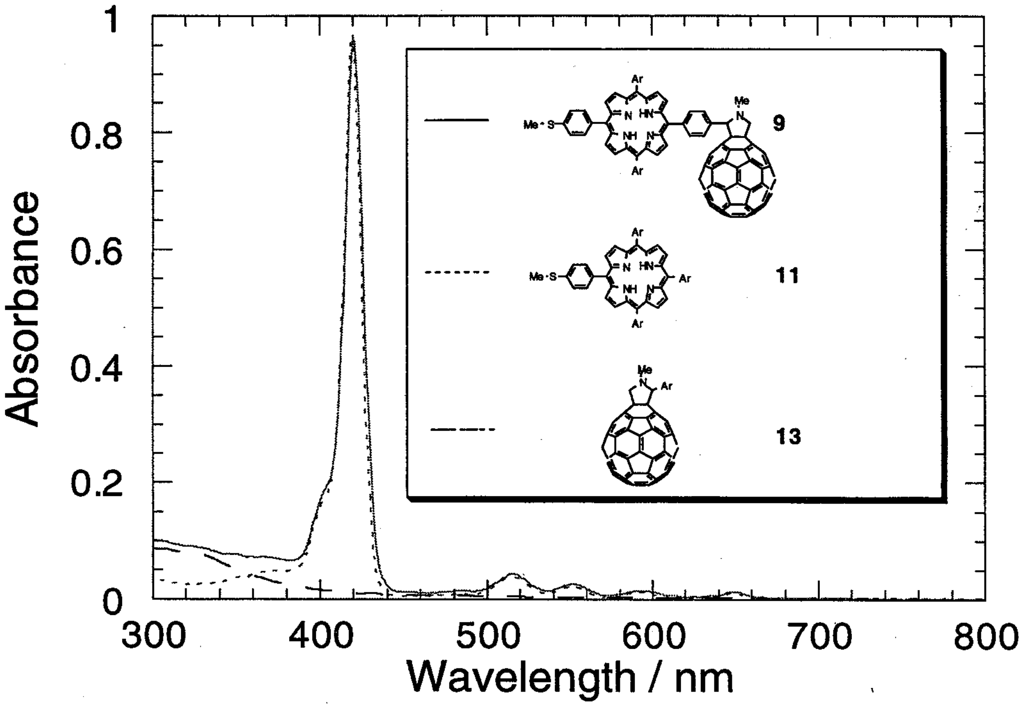
1.81μM in THF

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



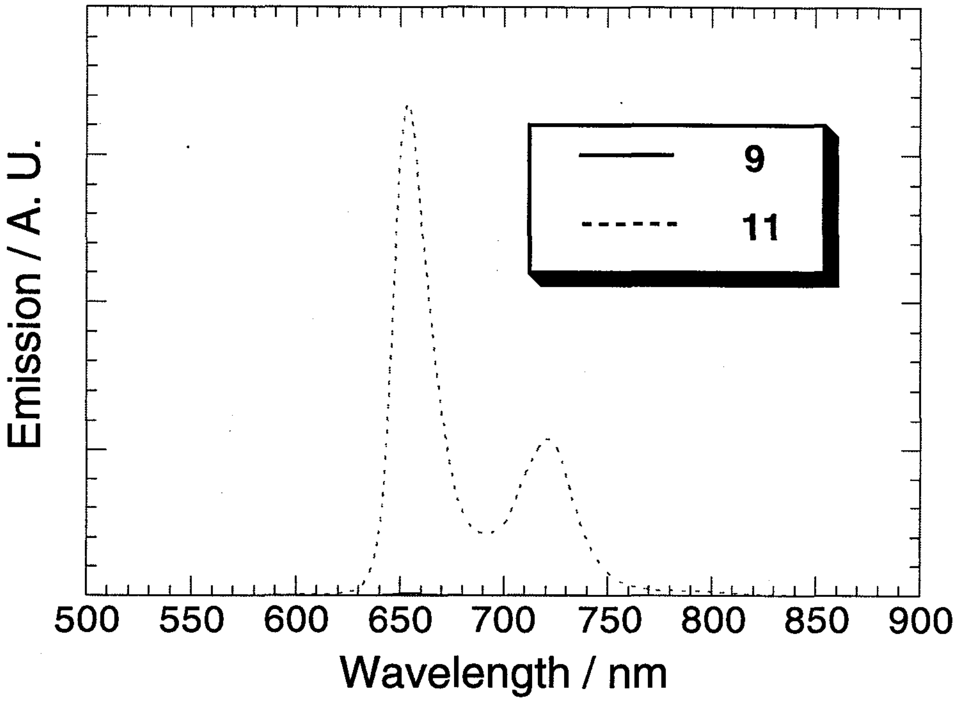
1.81μM in THF

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

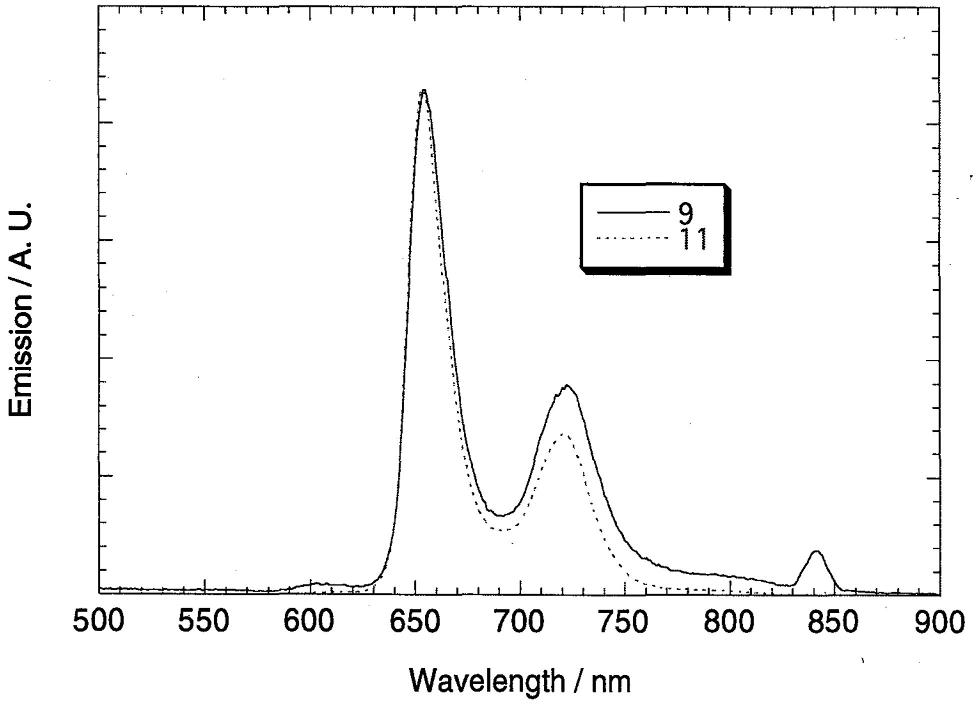


1.81μM in THF

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

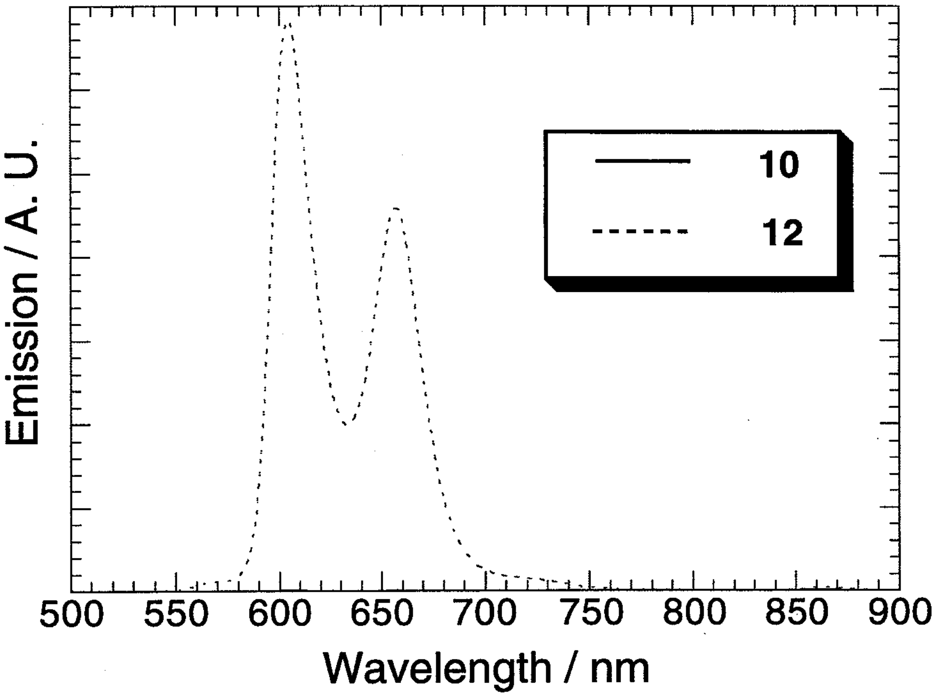


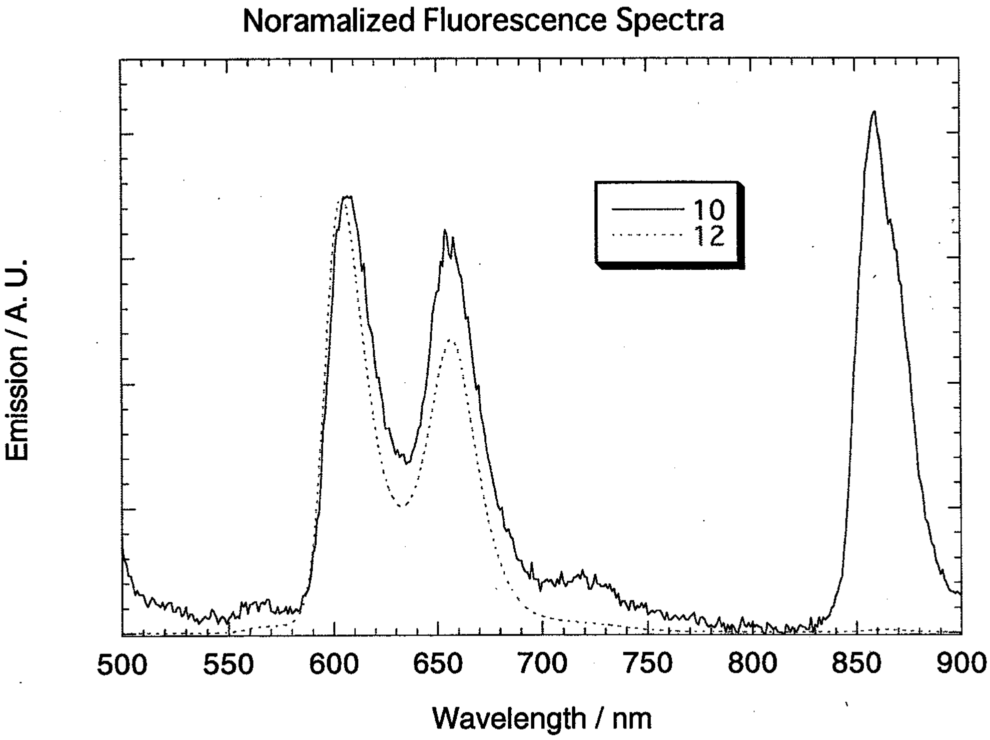
Normalized Fluorescence Spectra



1.81 μM in THF, Excitation : 420nm

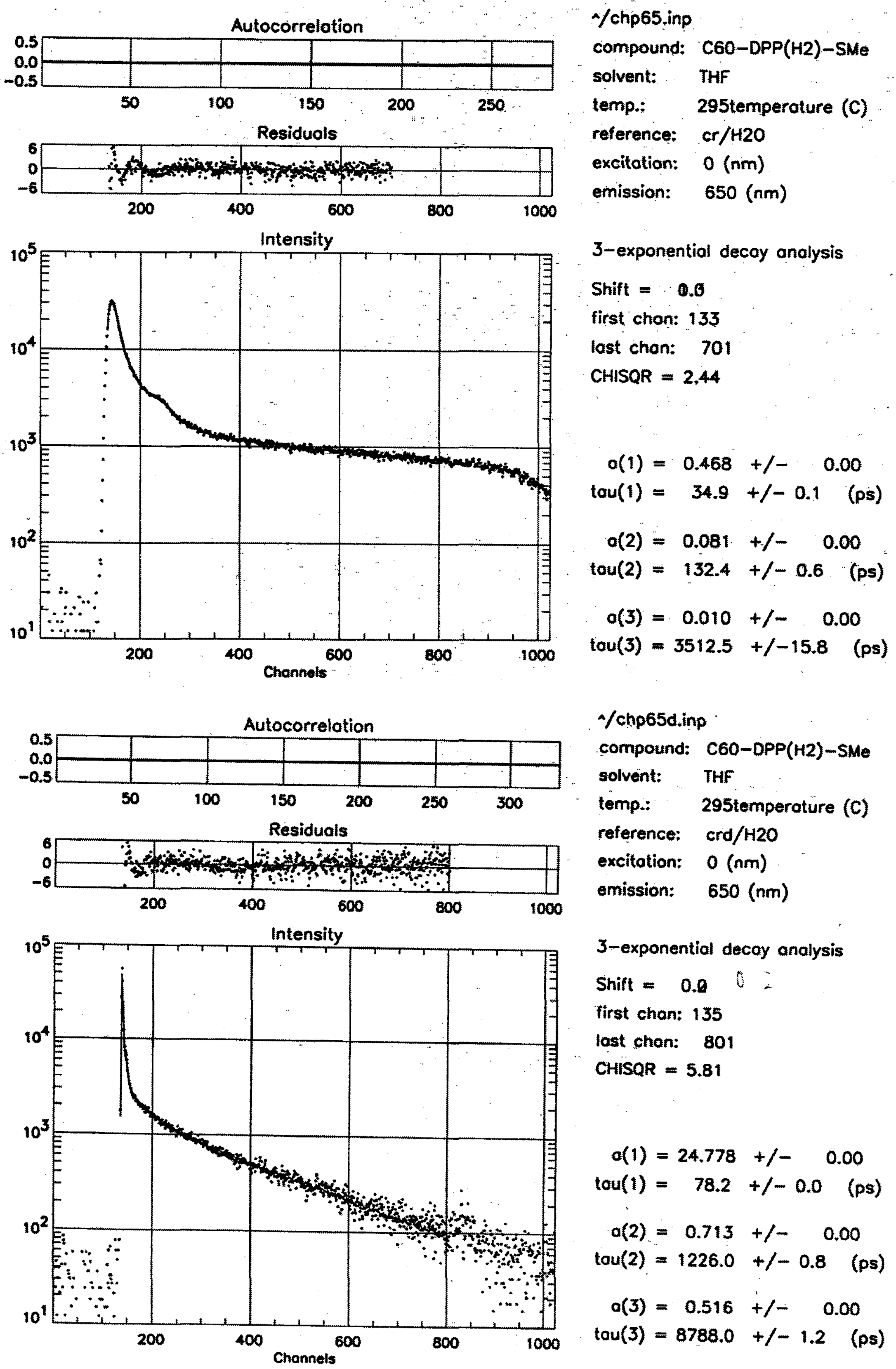
Figure 13 Fluorescence Spectra of **9** and **11**





1.81 μM 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

  a(1) =  0.468  +/-    0.00
tau(1) =   34.9  +/- 0.1   (ps)

  a(2) =  0.081  +/-    0.00
tau(2) =  132.4  +/- 0.6   (ps)

  a(3) =  0.010  +/-    0.00
tau(3) = 3512.5  +/-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

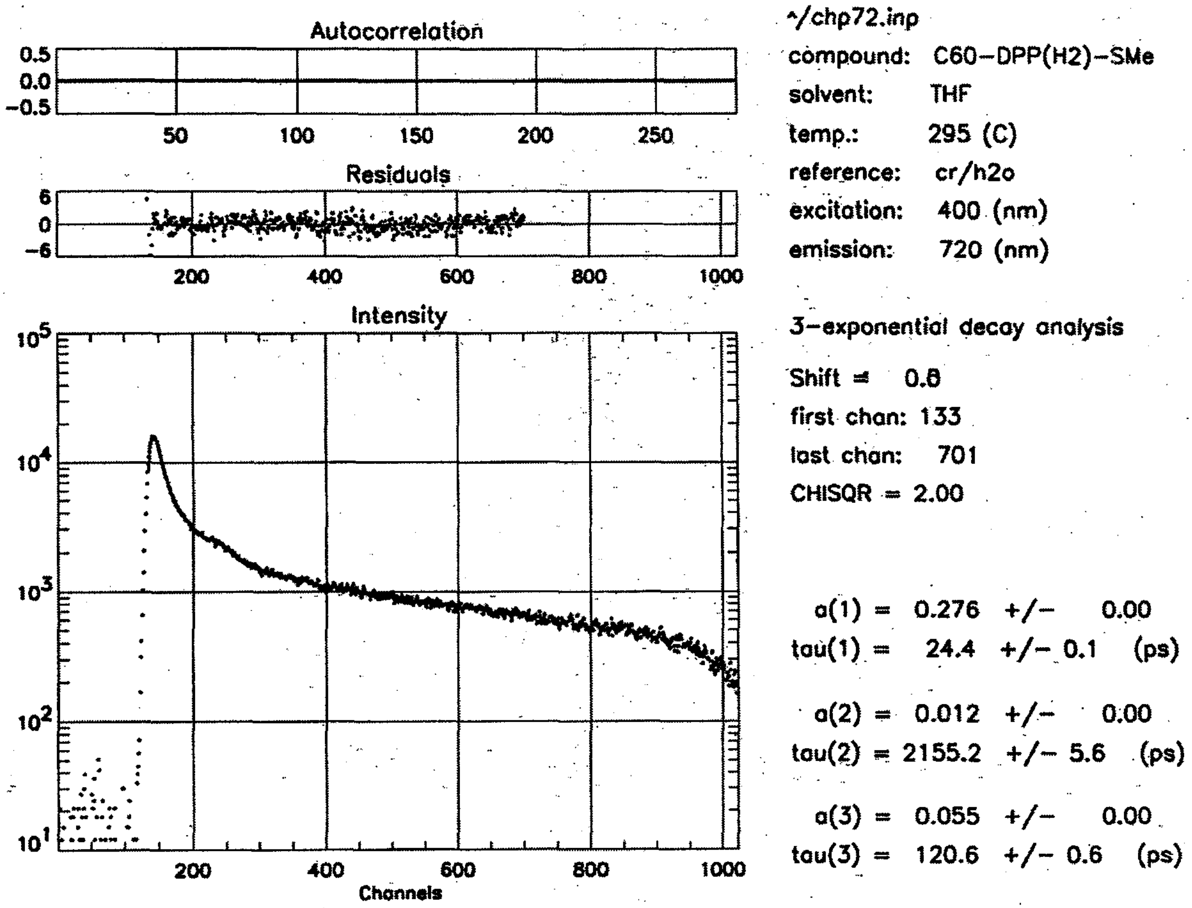
Shift =  0.0
first chan: 135
last chan:  801
CHISQR = 5.81

  a(1) = 24.778  +/-    0.00
tau(1) =   78.2  +/- 0.0   (ps)

  a(2) =  0.713  +/-    0.00
tau(2) = 1226.0  +/- 0.8   (ps)

  a(3) =  0.516  +/-    0.00
tau(3) = 8788.0  +/- 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

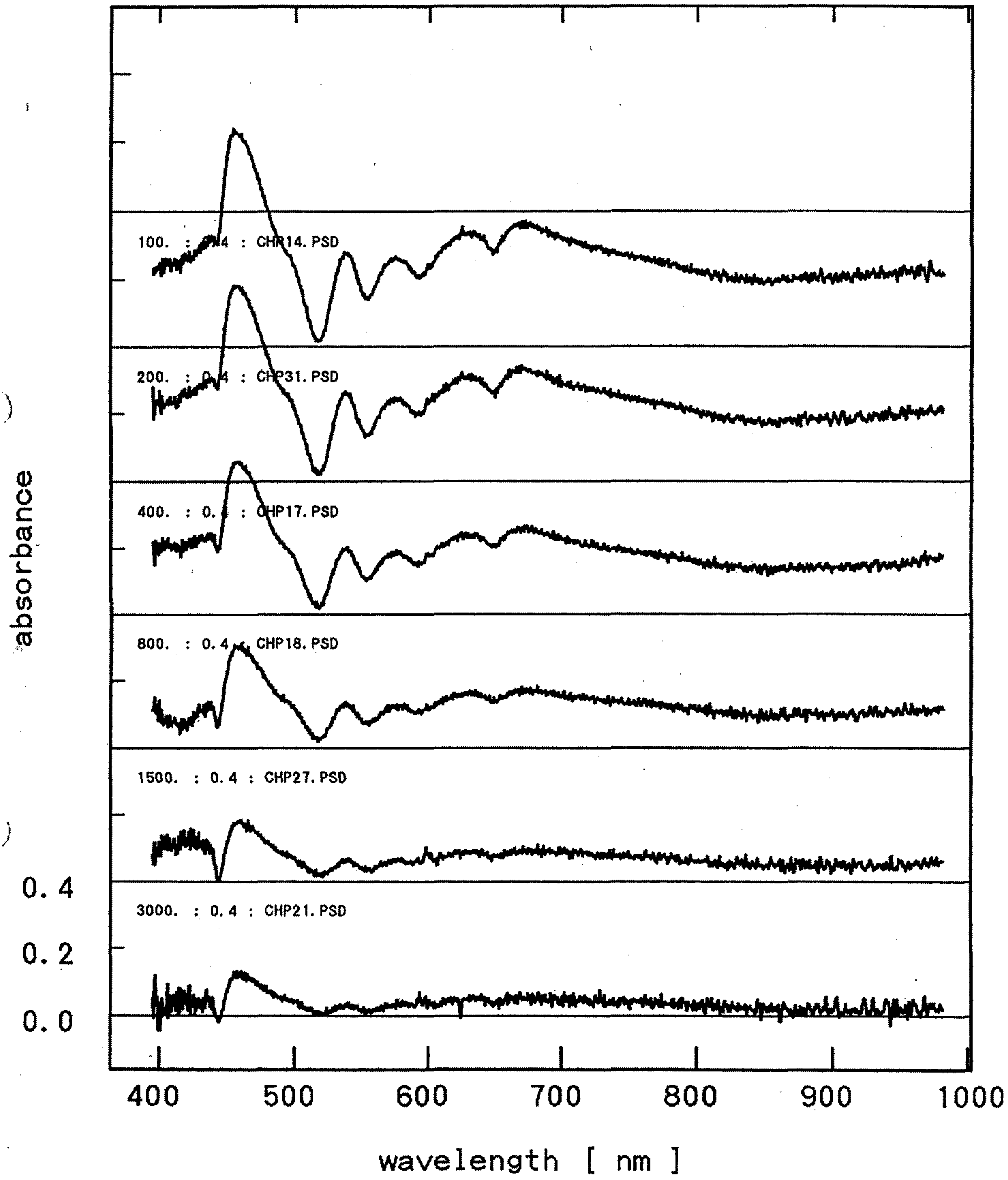
Shift =   0.8
first chan: 133
last chan:    701
CHISQR = 2.00


  a(1) =  0.276  +/-    0.00
tau(1) =   24.4  +/- 0.1   (ps)

  a(2) =  0.012  +/-    0.00
tau(2) = 2155.2  +/- 5.6   (ps)

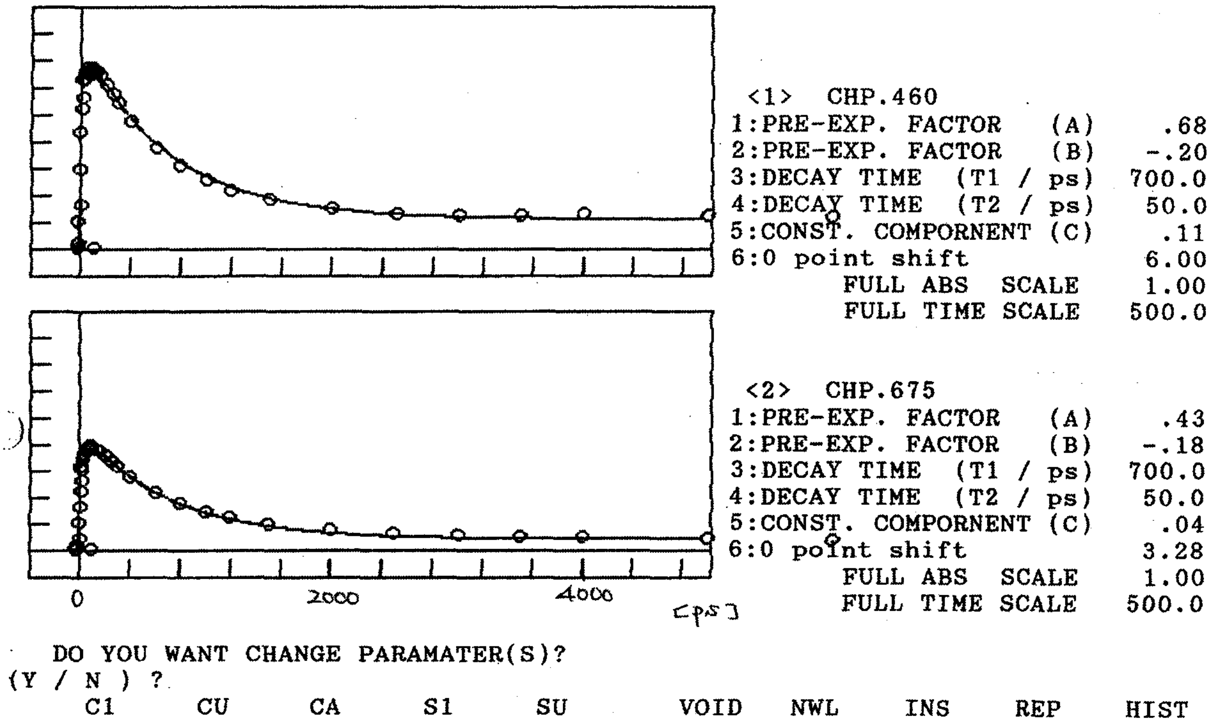
  a(3) =  0.055  +/-    0.00
tau(3) =  120.6  +/- 0.6   (ps)
```

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. COMPORNENT (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. COMPORNENT (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
```

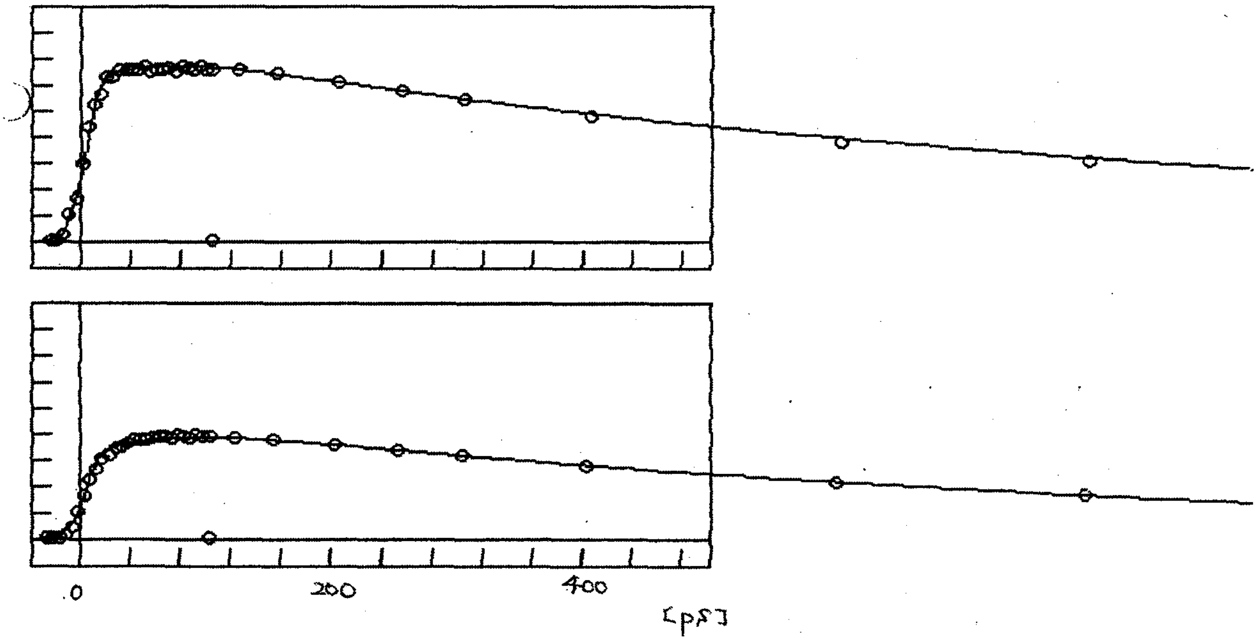
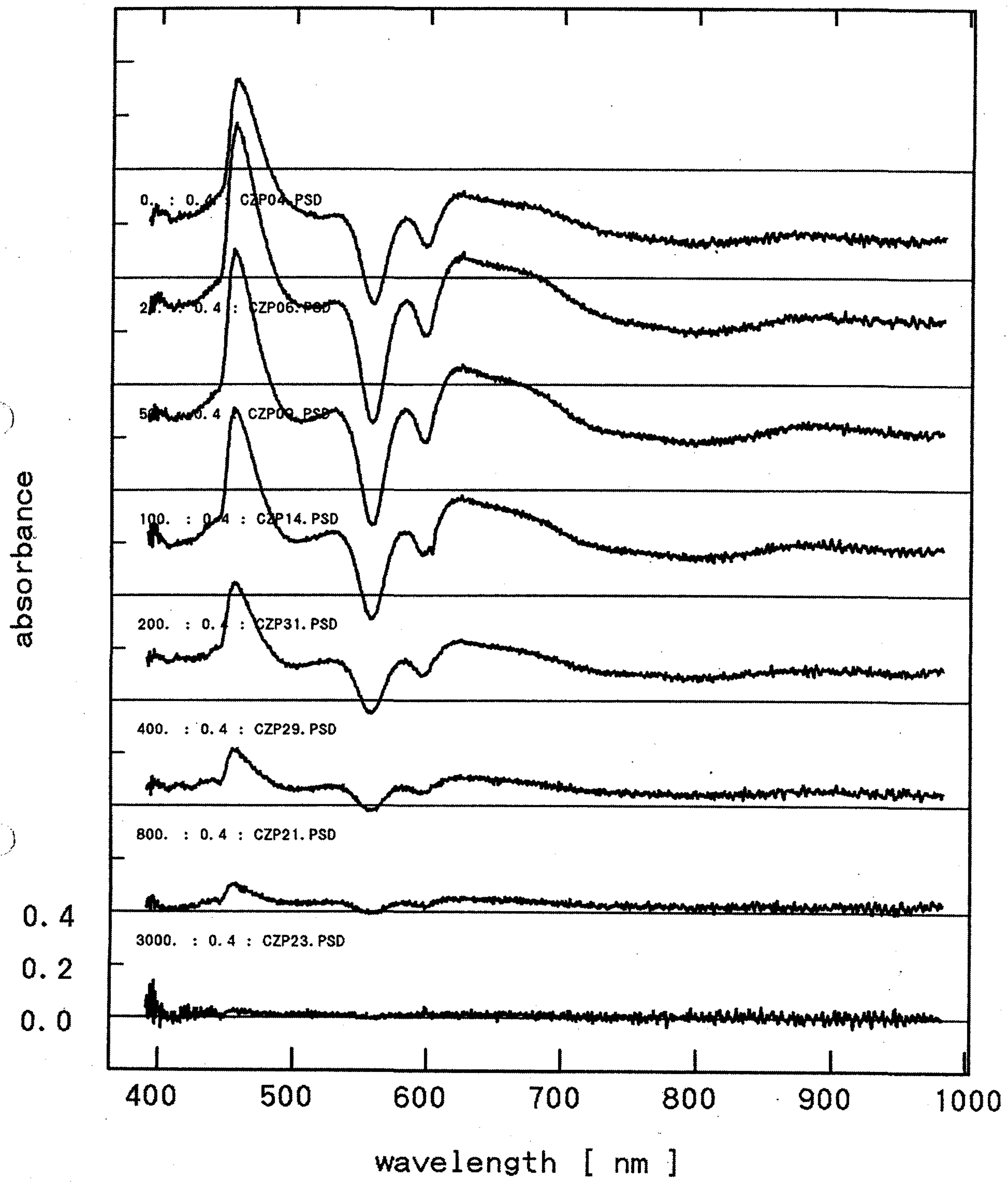
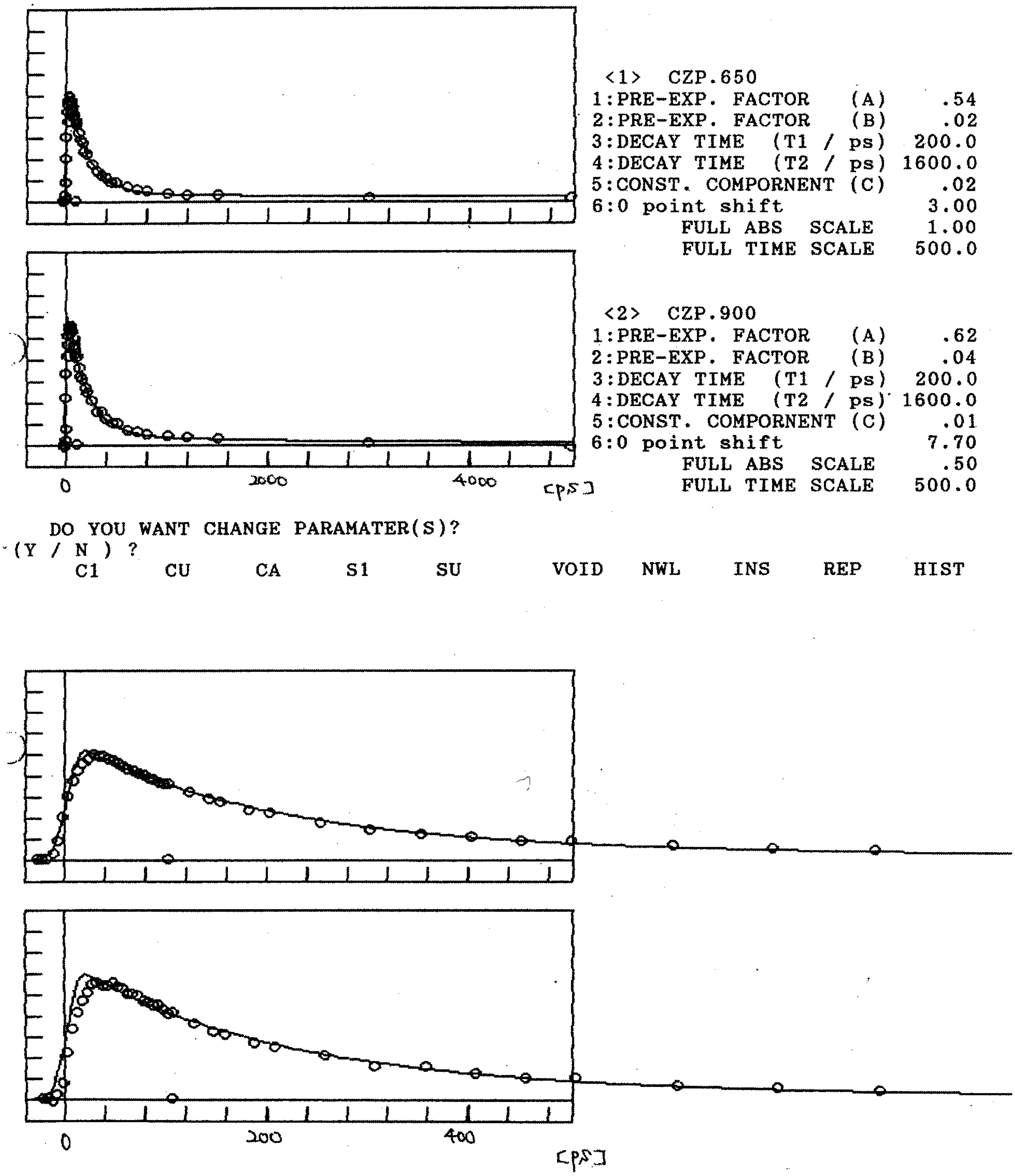


Figure 14-4 Analysis of Time-Resolved Transient Absorption Spectra of **9**



21 30 06-02-'96 01:35
CZP04.prn

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

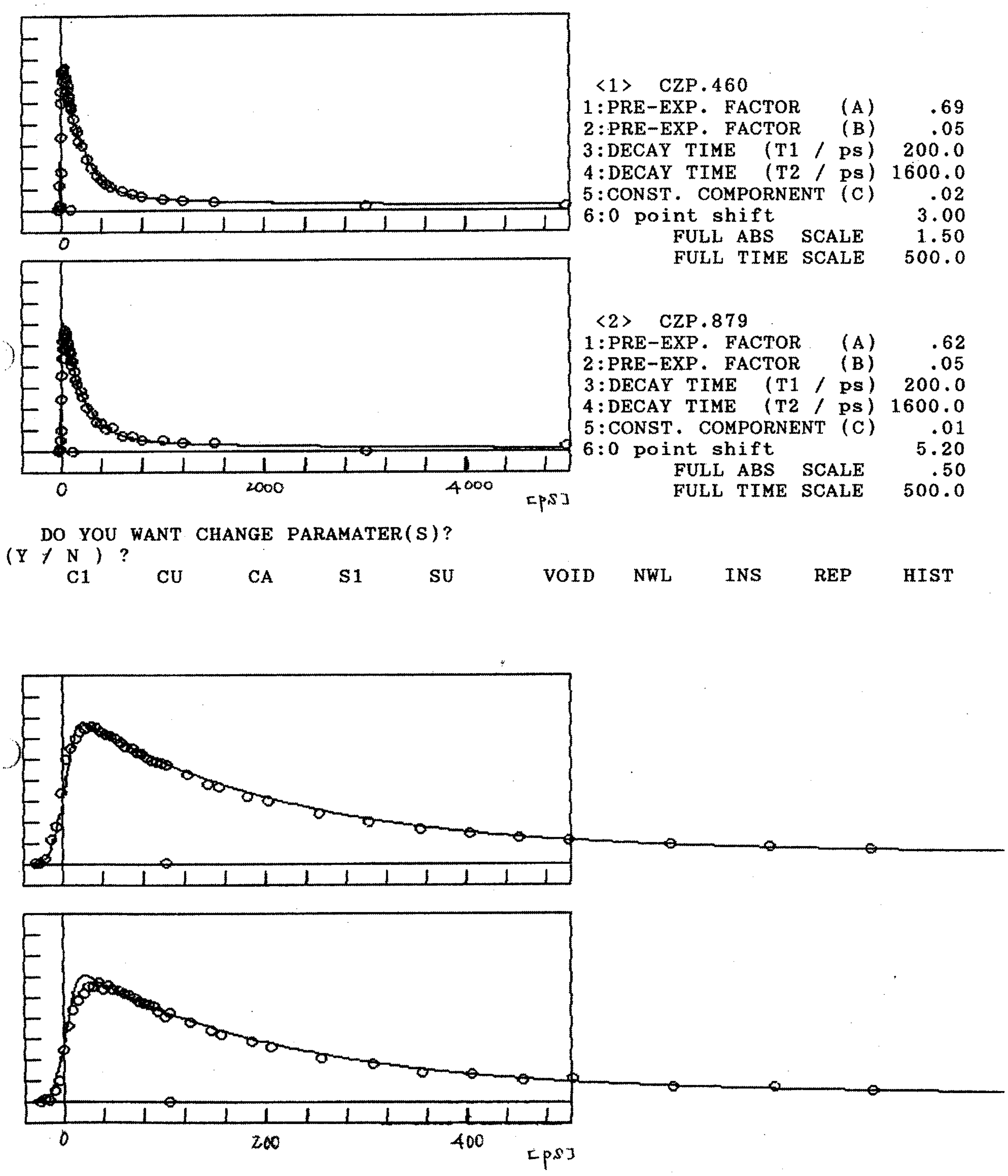


```
 <1>  CZP.650
1:PRE-EXP. FACTOR    (A)     .54
2:PRE-EXP. FACTOR    (B)     .02
3:DECAY TIME   (T1 / ps)   200.0
4:DECAY TIME   (T2 / ps)  1600.0
5:CONST. COMPORNENT (C)      .02
6:0 point shift             3.00
      FULL ABS  SCALE       1.00
      FULL TIME SCALE      500.0

 <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**

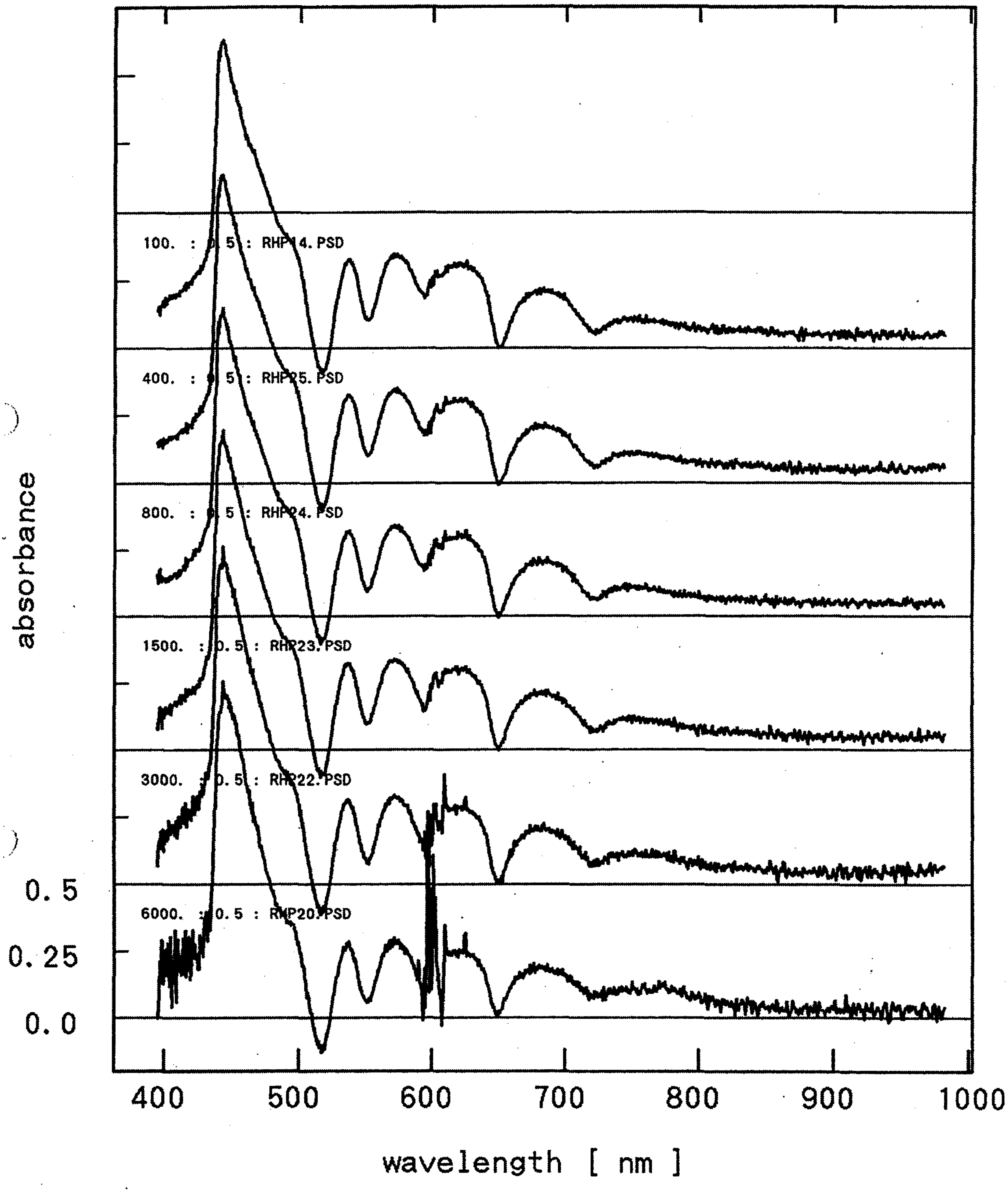


```
<1>  CZP.460
1:PRE-EXP. FACTOR    (A)     .69
2:PRE-EXP. FACTOR    (B)     .05
3:DECAY TIME   (T1 / ps)   200.0
4:DECAY TIME   (T2 / ps)  1600.0
5:CONST. COMPORNENT (C)      .02
6:0 point shift             3.00
       FULL ABS  SCALE      1.50
       FULL TIME SCALE     500.0

<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. COMPORNENT (C)      .01
6:0 point shift             5.20
       FULL ABS  SCALE       .50
       FULL TIME SCALE     500.0

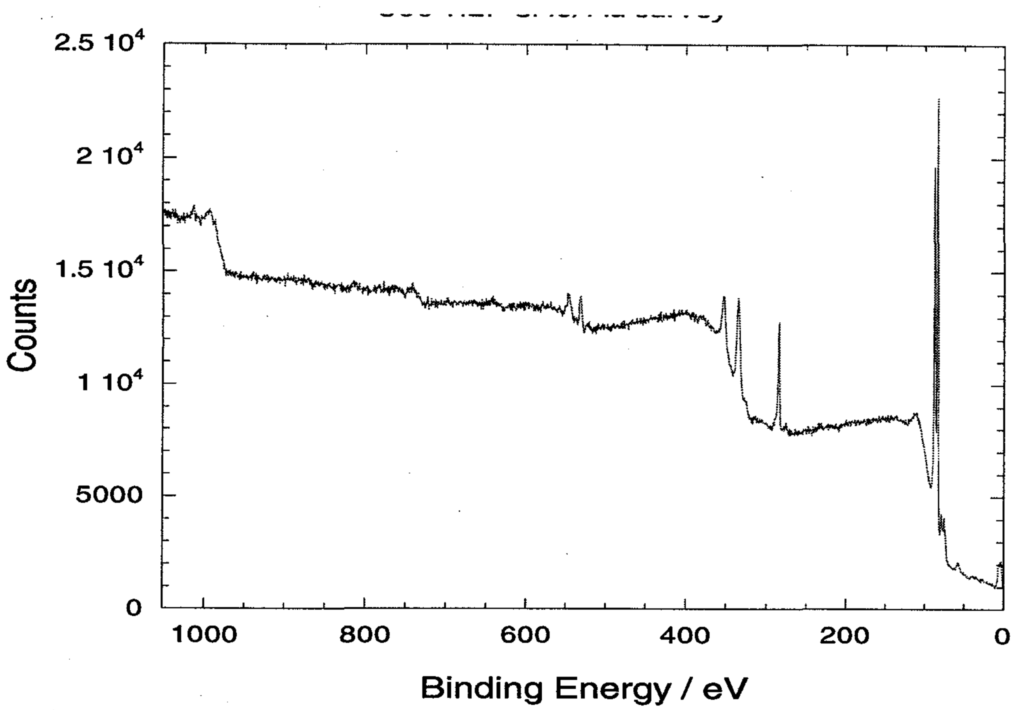
  DO YOU WANT CHANGE PARAMATER(S)?
(Y / N ) ?
     C1      CU      CA      S1      SU        VOID    NWL     INS     REP     HIST
```

Figure 14-7 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**



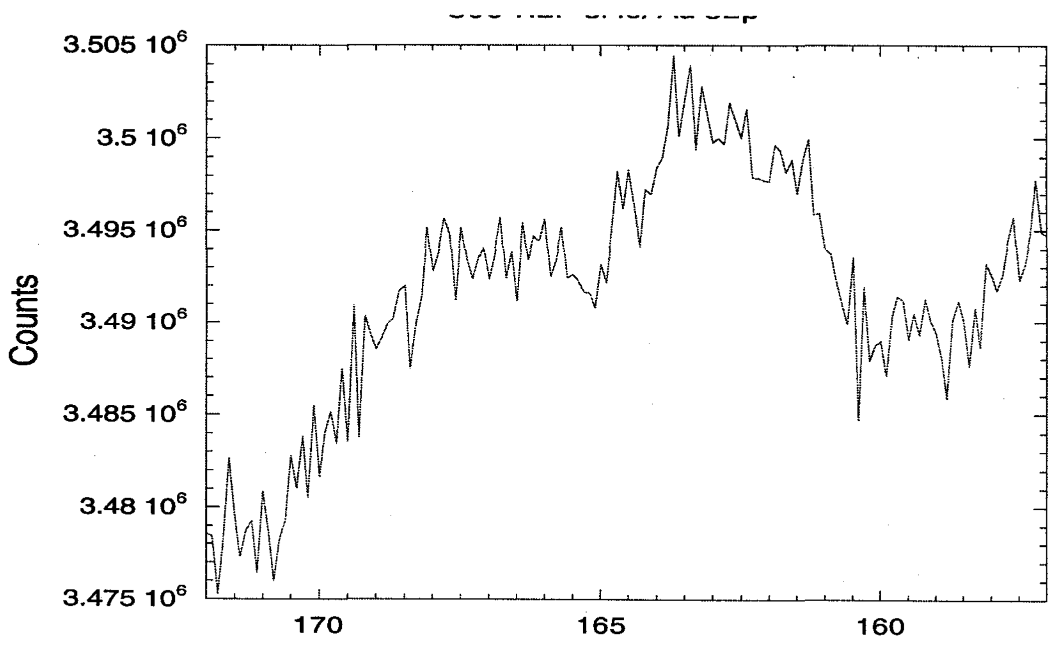


Figure 15 X-ray Photoelectron Spectra of **9** / Au

X-ray Photoelecron Spectroscopy

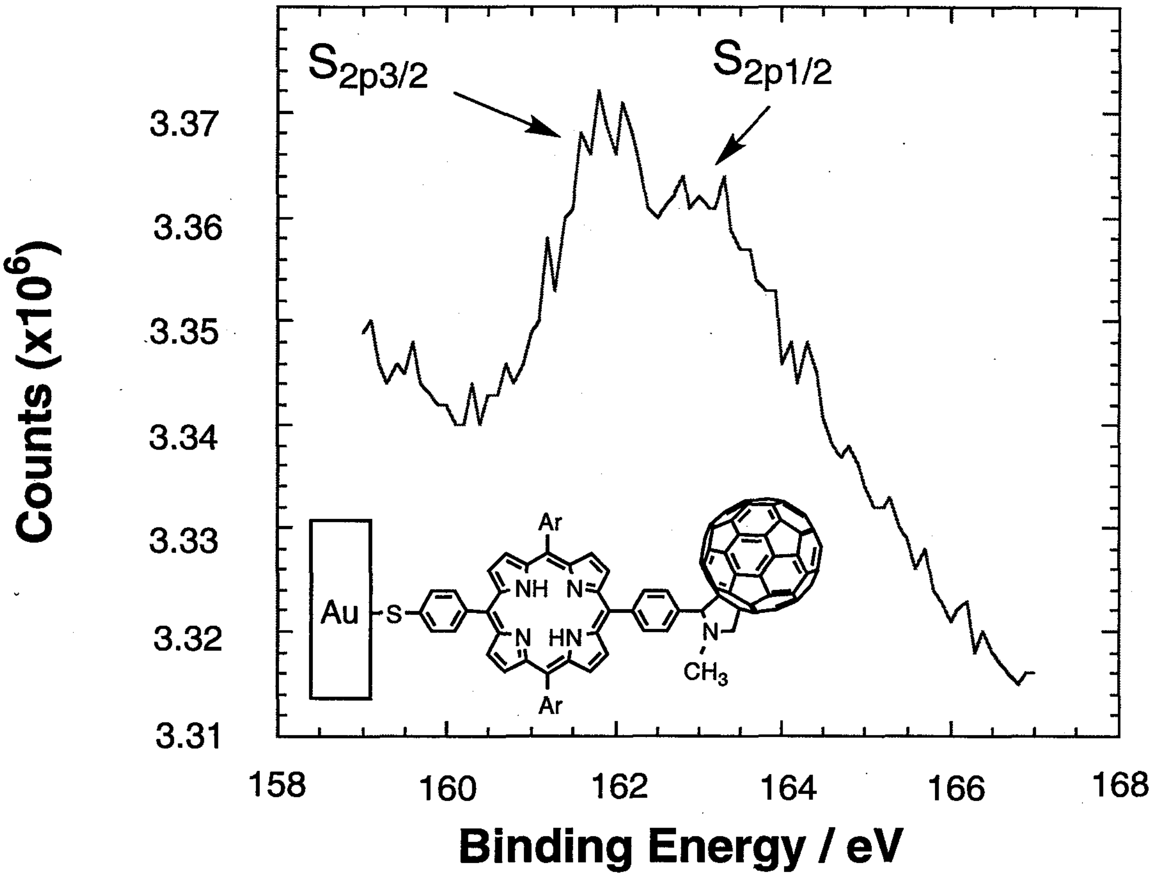


Figure 15-2 X-ray Photoelectron Spectra of **9** / Au

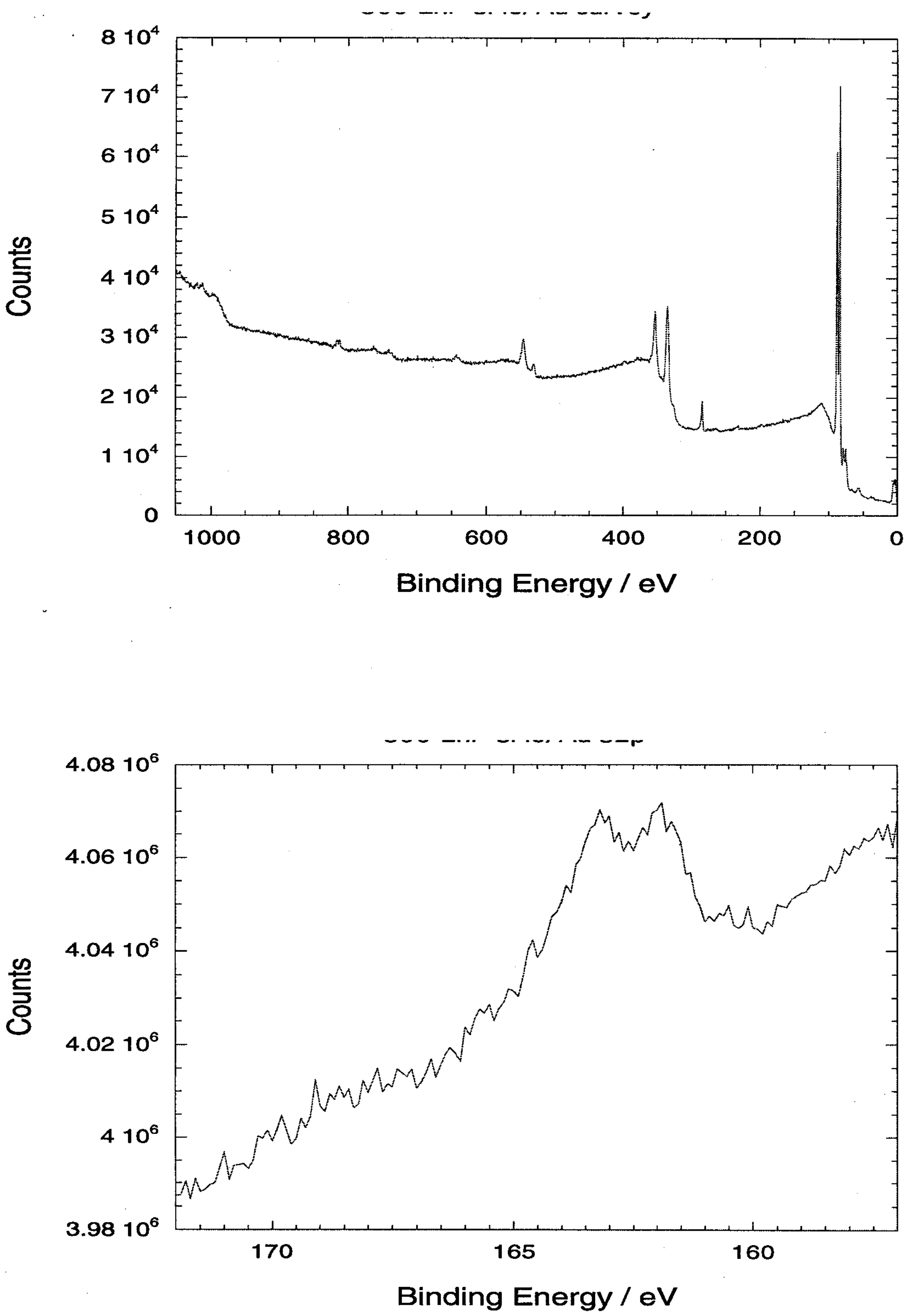


Figure 15-3 X-ray Photoelectron Spectra of **10** / Au

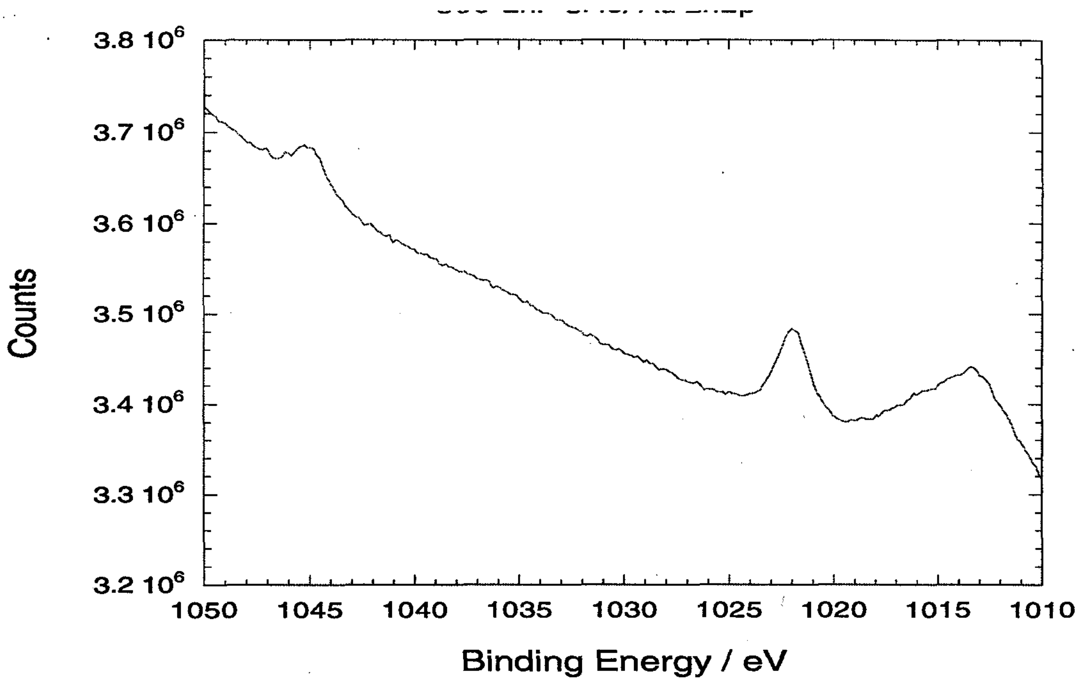
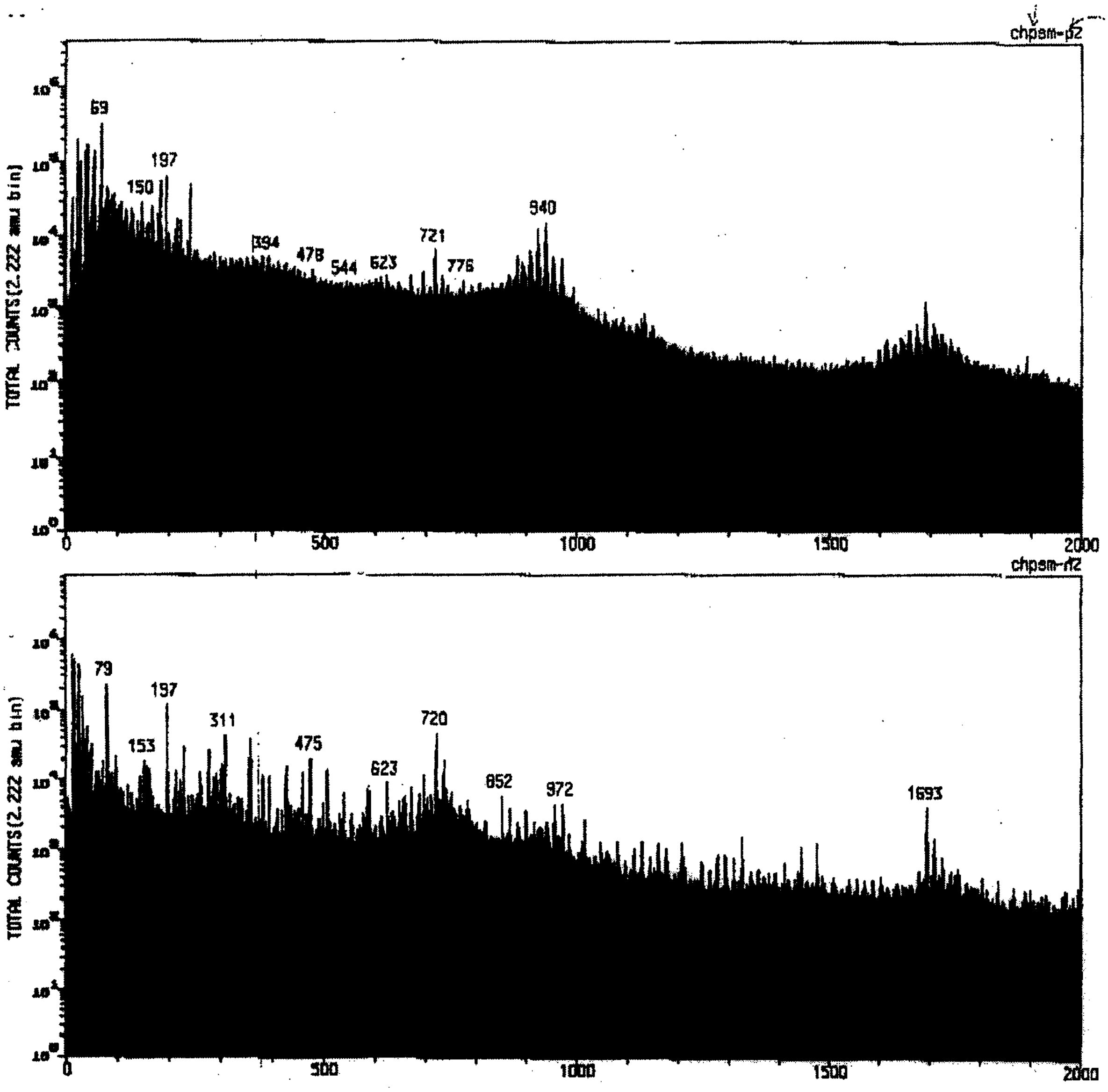


Figure 15-4 X-ray Photoelectron Spectra of **10** / Au



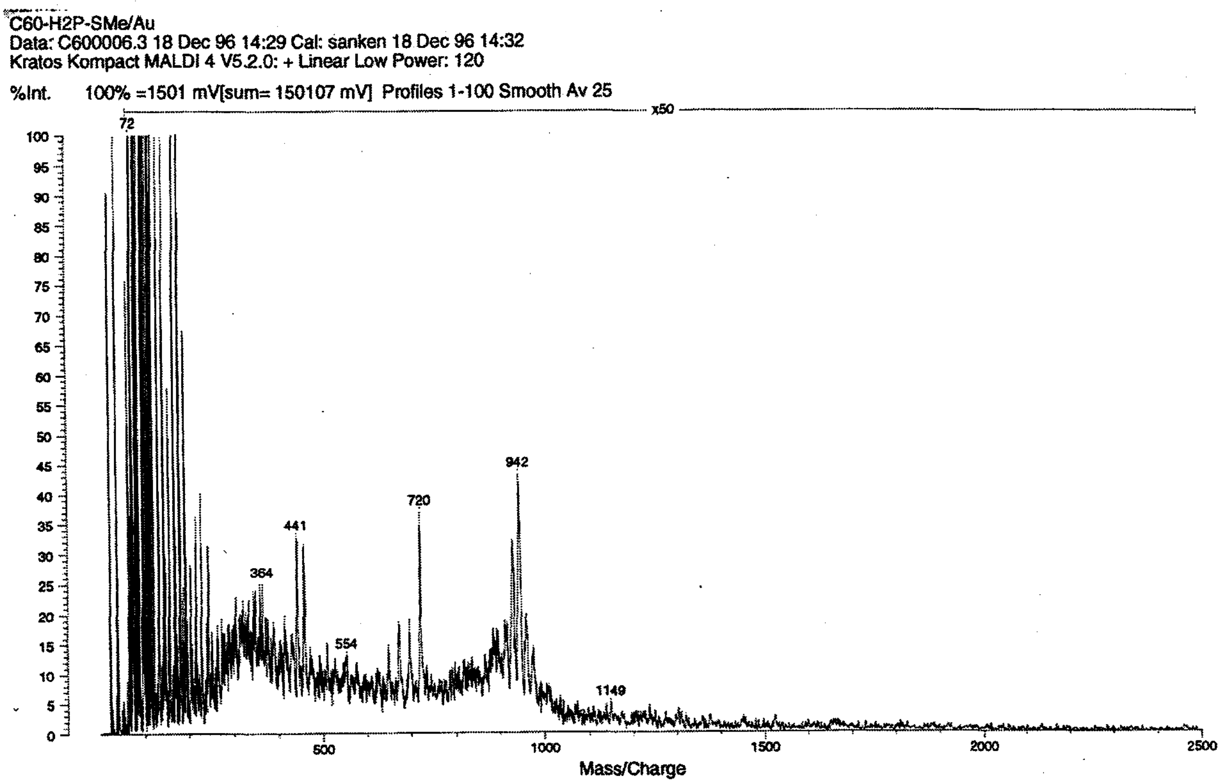
FILE NAME: chpsm-p2 DATE : 1 Nov 96 11:04 ACQUISITION TIME: 6.0 MIN. TOTAL INTEGRAL : 4192768

+ 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 NI FlyBack

FILE NAME: chpsm-n2 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 NI FlyBack

Figure 16 Ga+ Ionization TOF Mass Spectra of **9** / Au



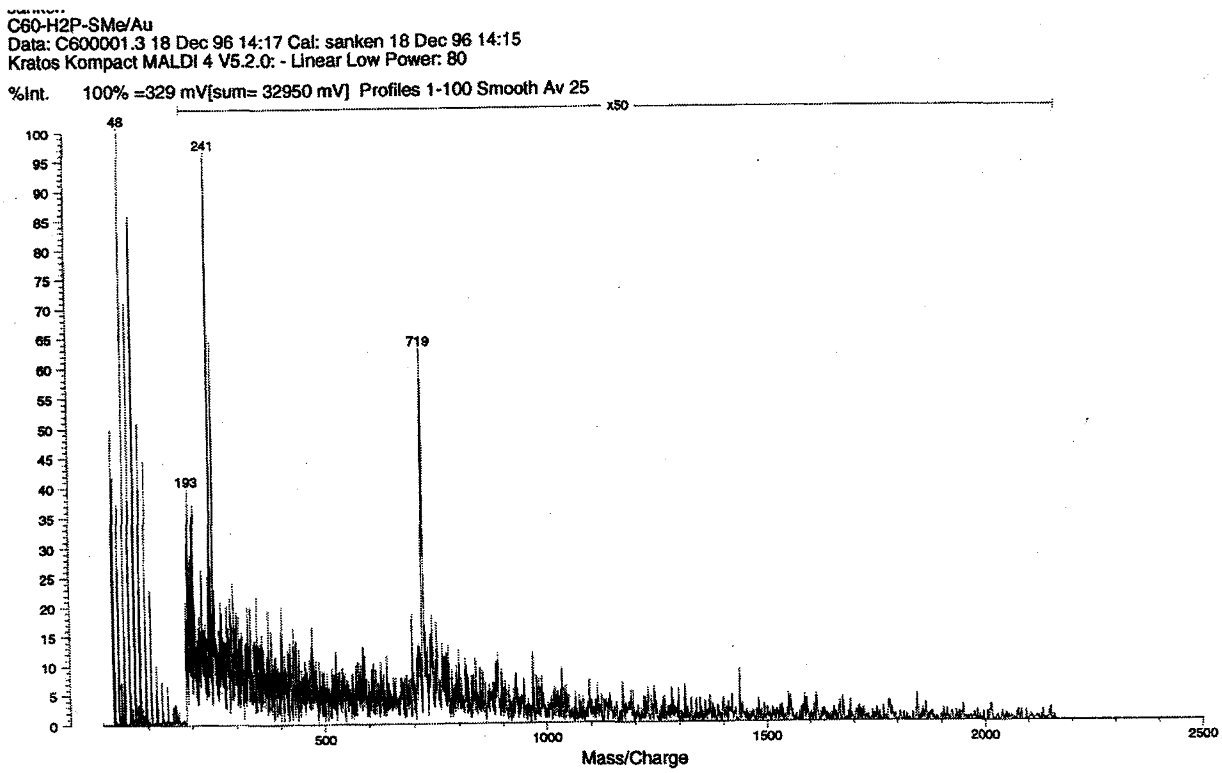


Figure 17 Laser Ionization TOF Mass Spectra of **9** / Au

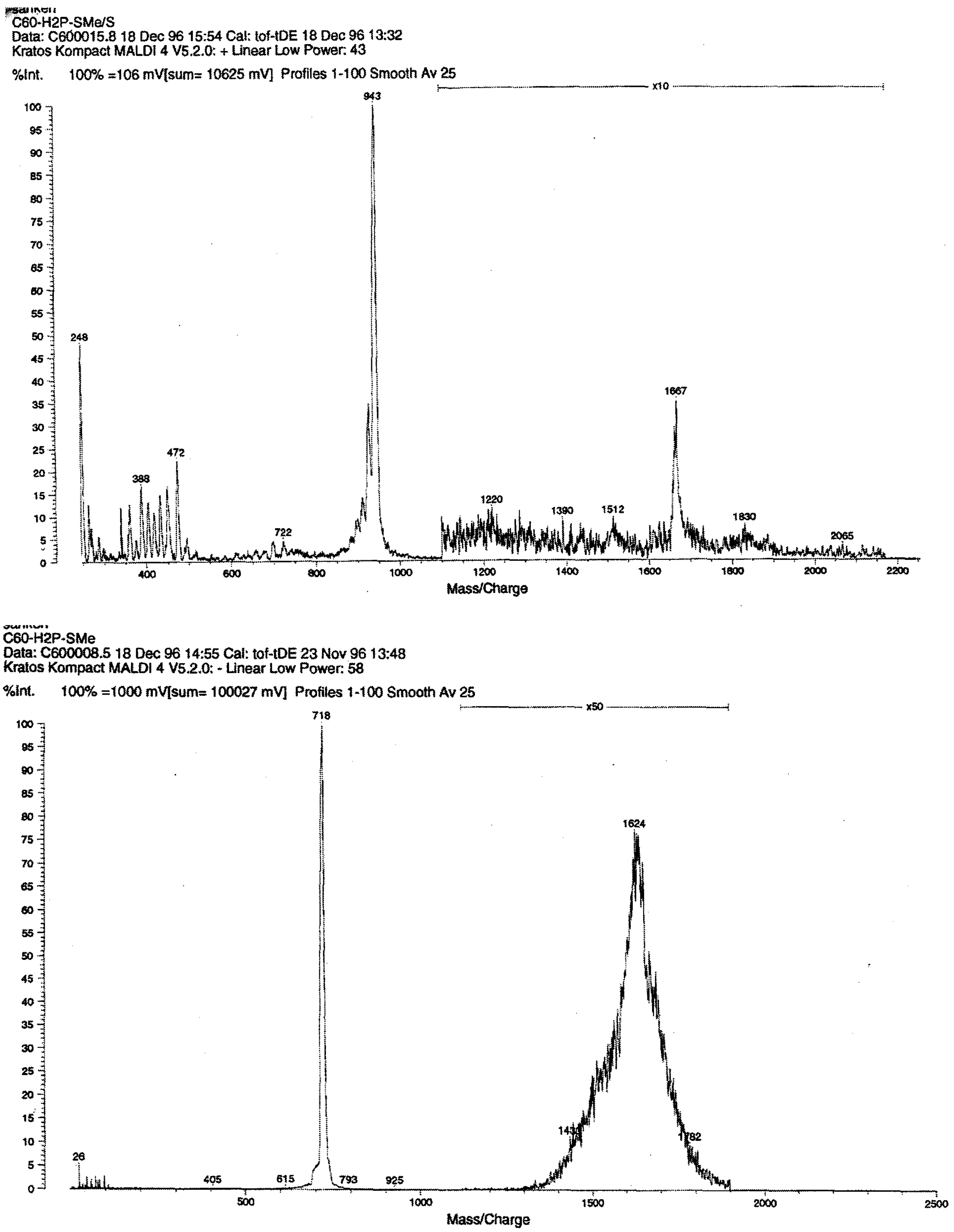


Figure 17-2 Laser Ionization TOF Mass Spectra of **9** without Matrix

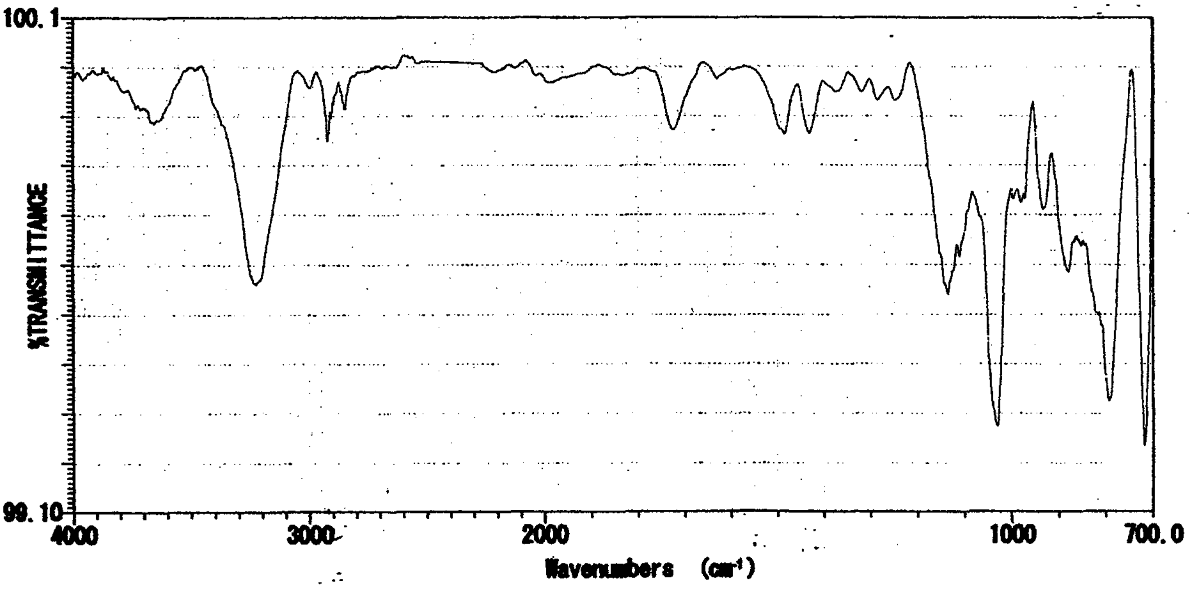
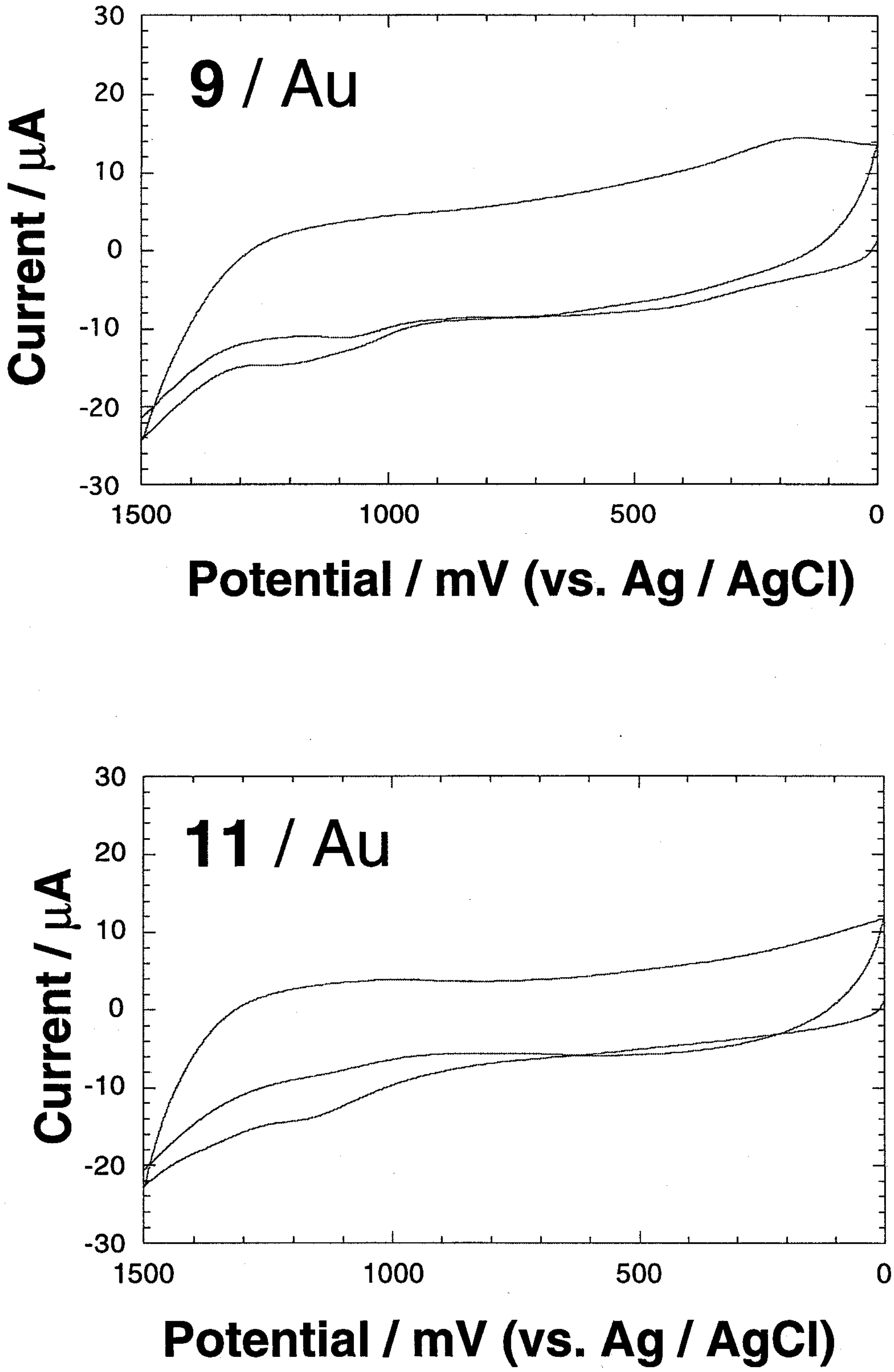


Figure 18 Reflective Absorption Spectra of **11** / Au



Electrolyte : 0.1M n-Bu_4NPF_6 in CH_2Cl_2, referenece electrode : Ag / AgCl, counter electrode : Pt wire, scan rate : 500mV / sec

Figure 19 Cyclic Voltametry

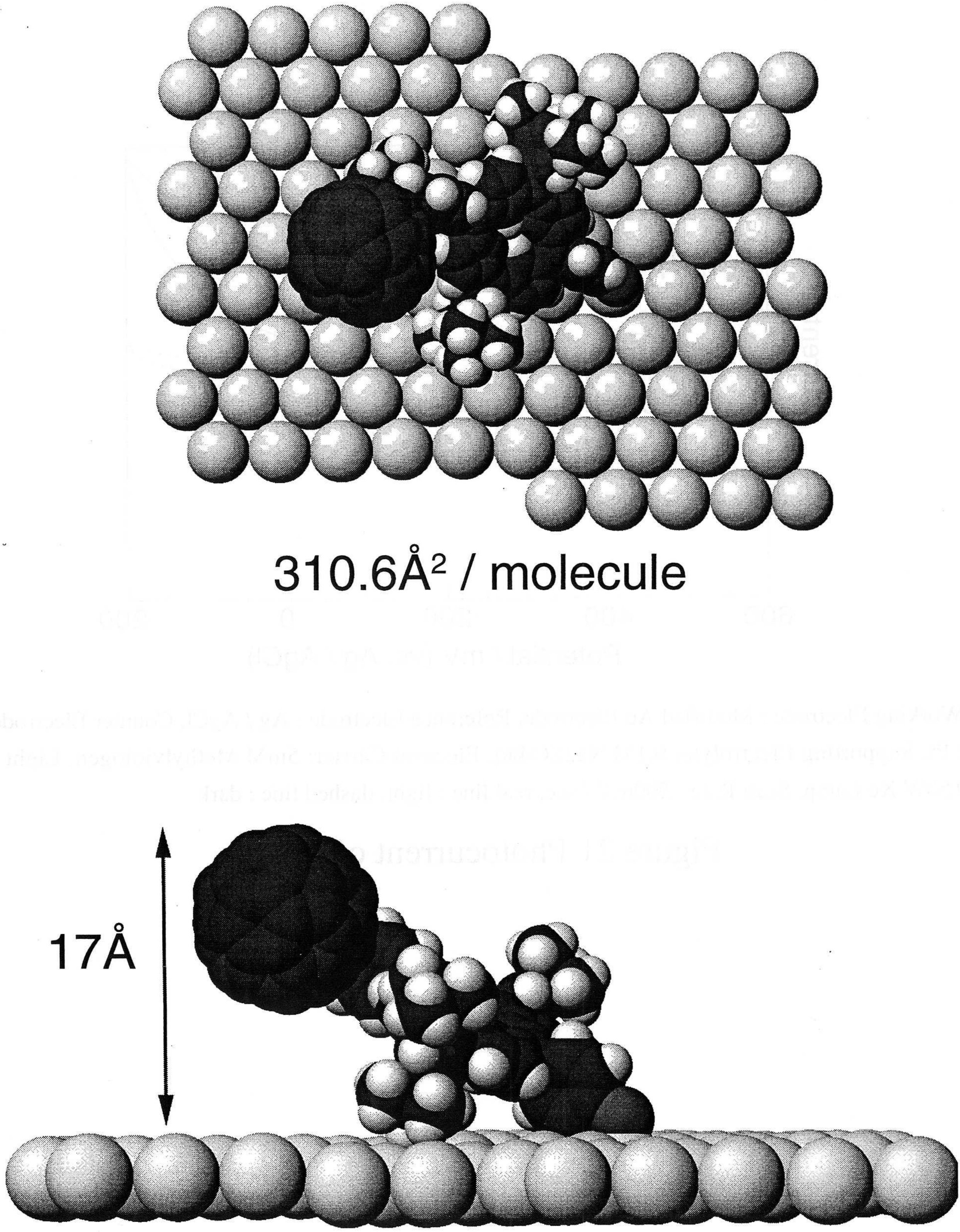
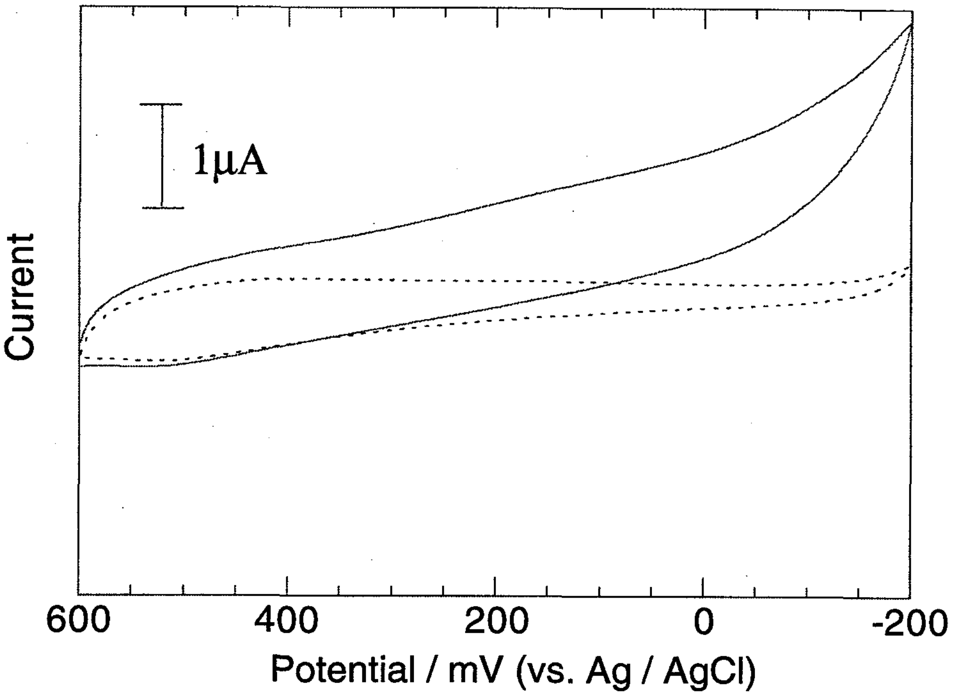
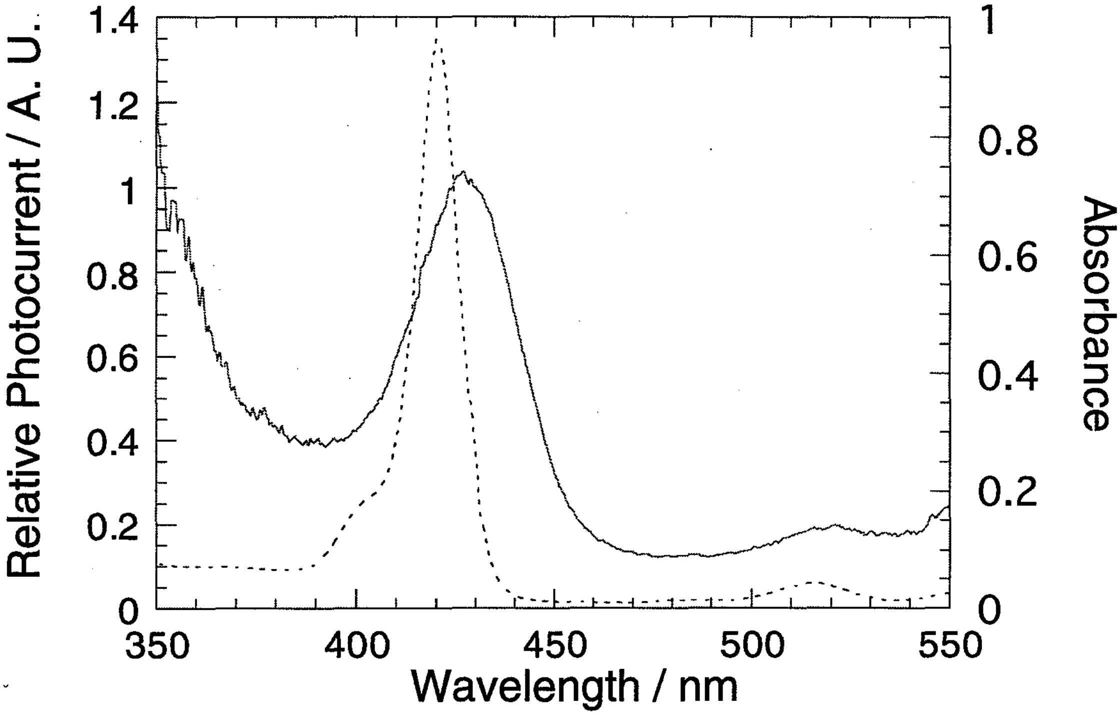


Figure 20 Molecular Mechanics Calculations of **9** / Au



Working Electrode : Modified Au Electrode, Reference Electrode : Ag / AgCl, Counter Electrode : Pt, Supporting Electrolyte: 0.1M Na2SO4aq, 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 Na2SO4aq, Electron Carrier: 5mM Methylviologen, Light : 300W Xe Lamp, Obserbed Potential : 0mV, real line : photocurrent of 9 / Au, dashed line : electronic absorption spectrum of 9 in THF

Figure 22 Action Spectrum of **9** / Au

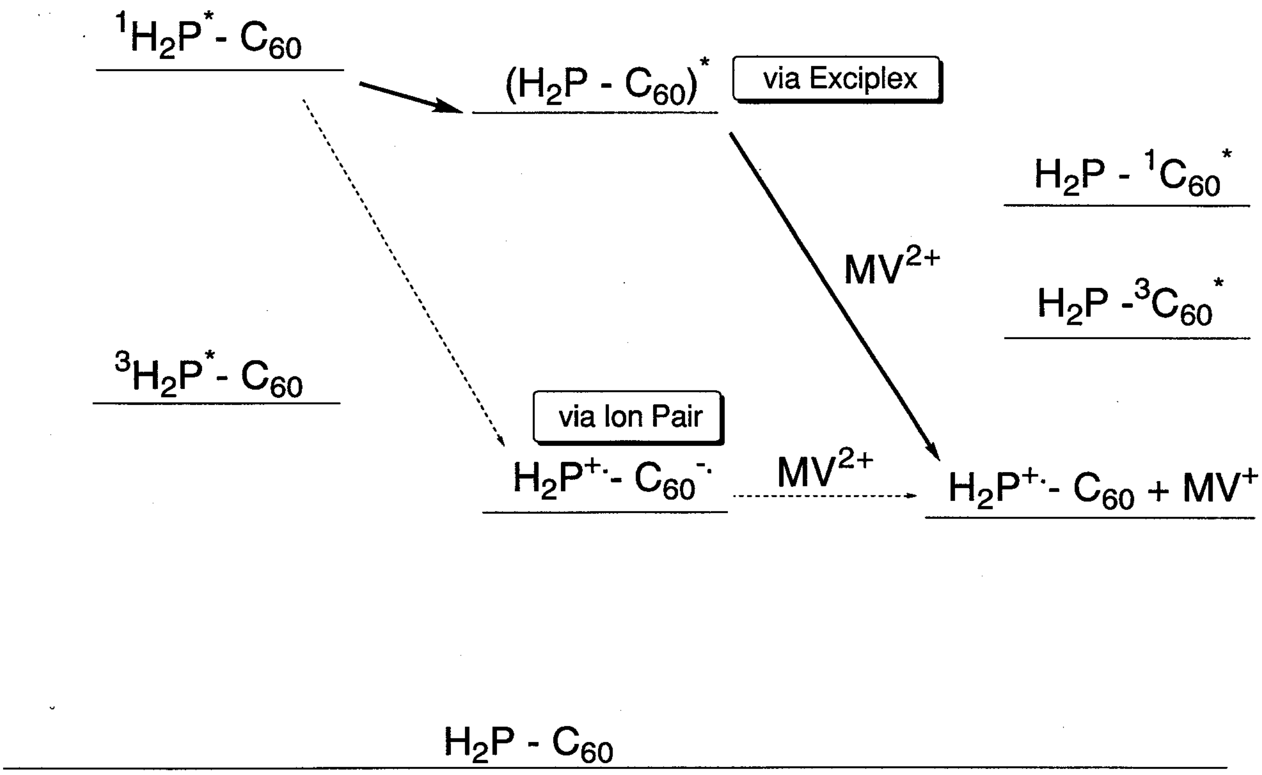


Figure 23 Possible Mechanism of Photocurrent Generation

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 μA 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_{60} 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_{60} 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_{60} 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.*