

氏 名 猪 野 大 輔

学位（専攻分野） 博士(理学)

学 位 記 番 号 総研大甲第789号

学位授与の日付 平成16年3月24日

学位授与の要件 先導科学研究科 光科学専攻

学位規則第4条第1項該当

学 位 論 文 題 目 Ultrafast electron transfer and relaxation dynamics  
at organic molecules-metal interfaces

論 文 審 査 委 員 主 査 助 教 授 高 木 紀 明  
教 授 松 本 吉 柔  
助 教 授 佃 達 哉  
研 究 員 宗 像 利 明 (理 化 学 研 究 所)

## 論文内容の要旨

Organic light emitting diodes (OLED) have attracted much attention since the first application of OLED in 1987. There have been extensive theoretical and experimental studies for an understanding of the physics of OLED. It has been suggested that excited states and electron dynamics in organic thin films and at metal interfaces are crucial to achieve high efficiency in the operation of OLED. However, the electronic states of organic molecules at metal interfaces, in particular, charged states such as electron affinity levels and their dynamics have not been thoroughly studied. Most of the studies on the dynamics of excited states and electron transfer at organic/metal interfaces have been derived from steady-state current-voltage characteristics. These results are often influenced by many other interface and bulk properties. Surprisingly we have little knowledge even on the affinity levels of organic molecules at interfaces and their energy alignments with respect to the Fermi level ( $E_F$ ) of metals, which are the most crucial point in basic science and practical applications. Therefore, it is vital to identify the electronic states of organic semiconductor molecules not only in thin films but also metal interfaces and to explore their ultrafast dynamics.

Given the perspective cited above, the aim of this thesis is to explore mainly three subjects regarding excited-state and electron dynamics in organic thin films and at metal interfaces:

- (i) Excited-state dynamics in organic thin films,
- (ii) Electronic structure at organic-molecule/metal interfaces,
- (iii) Ultrafast electron dynamics at organic-molecule/metal interfaces.

Organic materials employed in this study are  $\pi$ -conjugated molecules of tris-(8-hydroxyquinolate)-aluminum ( $Alq_3$ ) and 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA). They are archetype organic semiconductor molecules and have been extensively studied because of their unique features. To achieve the goals of this thesis, we employed femtosecond time-resolved two-photon photoelectron spectroscopy (TR-2PPE). TR-2PPE has the following unique capabilities: (1) direct observation of electrons dynamics at specific electron energy and momentum in the femtosecond time scale (2) high sensitivity to excited states at molecular-metal interfaces, (3) observation of electron transferred states, i.e. the electron affinity levels of organic molecules. TR-2PPE studies incorporated with various surface science techniques such as ultraviolet photoelectron spectroscopy (UPS), x-ray photoelectron spectroscopy (XPS) uncover not only electronic structures but also ultrafast electron dynamics at organic molecule-metal interfaces. The time-resolution of TR-2PPE experiments is drastically improved in this study by using a mirror dispersion controlled Ti:sapphire oscillator (pulse width  $\sim 12$  fs at 800 nm) or a home-made NOPA (pulse width  $\sim 12$  fs at 500  $\sim$  700 nm) as a light source.

- (i) Excited-state dynamics in organic thin films

Forrest and coworkers investigated the optical transitions of PTCDA in solution and thin films by measuring absorption and fluorescence spectra. In the  $S_1$  state manifold the fluorescence quantum efficiency reaches the maximum at  $h\nu = 2.1$  eV and drops sharply to  $< 1\%$  at  $h\nu > 2.2$  eV. This suggests that non-radiative surface recombination of excitons is responsible for the low fluorescence quantum efficiency of the  $S_1$  state. However, there have been no direct measurements of the decay dynamics of the  $S_1$  and higher-lying excited states. This thesis describes the ultrafast excited-state dynamics in PTCDA thin films. The energy relaxation of vibrational states in the  $S_1$  manifold manifests itself in the time-dependent energy shift of

2PPE signals attributed to them. The lifetime of the nearly radiationless  $S_1$  state is determined to be  $360 \pm 12$  fs, which is about four orders of magnitude shorter than the energy dissipation channel for charge-transfer excitons via fluorescence.

(ii) Electronic structure at organic-molecule/metal interfaces

In previous studies on the electronic structures of organic molecules, the energy alignment at metal interfaces has been discussed by the experimental results based on electron spectroscopy for occupied states and absorption spectroscopy for the HOMO-LUMO transition. This approach usually leads to misleading conclusions. Thus, we observed directly the energy level of an affinity level at Alq<sub>3</sub>/metal interfaces and explored how it depends on metal substrates of Cu and Au. The affinity levels of Alq<sub>3</sub> were observed at 2.8 eV for Cu(111) and 3.8 eV for Au(111) above  $E_F$ . In both cases, the energy position of the affinity level with respect to HOMO is very similar to that of thin films, indicating that the interaction between Alq<sub>3</sub> and surface atoms is very small. The binding energy of the affinity level with respect to the vacuum level is independent of the metal substrates used in this study. Therefore, the affinity level is pinned to the vacuum level. For Alq<sub>3</sub>/Cu(111), the energy of the affinity level decreases with increasing the coverage due to the polarization effects of surrounding molecules. From the combination of angle- and time-resolved measurements, we concluded that the affinity level is spatially localized in individual molecules.

(iii) Ultrafast electron dynamics at organic-molecule/metal interfaces

The rate of electron transfer is governed by the electronic coupling strength between donors and acceptors. Recently ultrafast spectroscopy incorporated with various surface science techniques has been developed to explore the interfacial electron transfer on metal or semiconductor surfaces. However, our knowledge is mostly limited in small molecules such as CO, H<sub>2</sub>O and C<sub>6</sub>F<sub>6</sub>. Electron transfer dynamics from metals to large organic molecules relevant to organic semiconductor devices has been still unclear. Thus, we observed on the ultrafast electron transfer dynamics at Alq<sub>3</sub>/metal interfaces in the femtosecond timescale. This is the first spectroscopic study of interfacial electron dynamics by employing a practical and a promising organic molecule that is characterized by the large molecular size of 10 Å with a complicated molecular structure.

From the time-resolved measurements, the lifetime of the affinity level is determined to be  $31 \pm 2$  fs for Alq<sub>3</sub>/Cu(111). On the other hand, the affinity level on Au(111) surface decays more rapidly, i.e. the lifetime is estimated to be  $< 10$  fs. The ultrafast decay rate on the Au(111) surface is attributed to the resonance coupling between the affinity level and Au sp-bands. The lifetime of the affinity level for Alq<sub>3</sub>/Cu(111) was measured at the range of 1 ~3 ML. The lifetime of the affinity level is independent of the coverage, indicating that excited electrons into the Alq<sub>3</sub> ultrathin film are localized at the first interface layer. Consequently, we proposed that the electron transport rate in Alq<sub>3</sub> thin films is limited by electron (polaron) hopping out of the first Alq<sub>3</sub> layer. The femtosecond dynamics of intramolecular structural relaxation and/or the reorientation of surrounding molecules triggered by the formation of a localized anion manifest themselves in a dynamic peak shift of the affinity level in the TR-2PPE spectra. A quasi-linear peak shift of -1200 meV/ps was observed for 1.1 ML Alq<sub>3</sub>/Cu(111). At the end this thesis summarizes the major results of the current study and provides future prospects.

## 論文審査結果の要旨

出願された博士論文は、有機半導体デバイスに関連した典型的な有機分子の薄膜やこれと金属との海面における電子構造、励起状態の緩和、電子移動ダイナミクスについての実験的研究成果をまとめたものである。次の2つの中心的な主題について詳しく述べられている。

(1) 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) 薄膜における電子励起状態緩和。PTCDA は多くの固体表面上で規則的に2次元配列する典型的な有機半導体分子の一つであり、その幾何学的及び電子的構造に関する多くの研究が成されてきた。しかし、薄膜の光学的特性などを支配する電子励起状態の動的過程については十分には知られていない。本論文では、フェムト秒時間分解2光子光電子分光(2PPE)により PTCDA 薄膜の電子構造を明らかにするとともに、電子励起状態寿命の実時間観測を行い、(a)S<sub>1</sub> 状態の寿命は CT 状態の蛍光寿命より4桁近く短い360fsであり、(b)励起エネルギーの増加に応じて励起寿命は急速に短くなり、S<sub>2</sub> 状態では70fsでいどになる、などの結果を得た。従って、S<sub>1</sub> 状態以上の電子状態では S<sub>0</sub> 状態への極めて早い内部転換が起きることが明らかになった。これらの結果は蛍光測定などで生えられない新規な知見である。

(2) tris 8-hydroxy-quinoline aluminum(Alq<sub>3</sub>)・貴金属界面における電子移動ダイナミクス。Alq<sub>3</sub> は有機エレクトロルミネッセンス素子における発光層、電子輸送層として用いられる代表的な分子である。金属界面での電子状態、及び、そこでの電子移動ダイナミクスは有機半導体デバイスの電子輸送に大きな影響を及ぼすと考えられるが、従来は単純な I-V 特性から間接的に議論されてきた。本論文では、銅と金の単結晶(111)表面上に Alq<sub>3</sub> を制御して堆積し、時間分解 2PPE により、電子移動ダイナミクスを直接明らかにした。まず、電子移動に直接関与する Alq<sub>3</sub> の負イオン状態が金属のフェルミ準位よりも約 3eV 上に位置しており、この寿命が Cu(111)表面では 31fs、Au(111)表面では<10fs という極めて短寿命であることを初めて見いだした。これは、Alq<sub>3</sub> バルク内での電子移動に比べて第一層にある負イオン状態から金属への逆電子移動が約 100 倍以上も速く起きることを意味する。また、負イオン状態は第一層にある個々の Alq<sub>3</sub> 分子に局在していることも明らかになった。さらに、負イオン形成に伴う構造変化により、電子状態が時間的に変化することを初めて見いだした。このような結果に基づき、電子輸送効率の向上のためにはこの負イオン状態の安定化・長寿命化が極めて重要であるという結論に達した。

本論文は、従来の観測では得られなかった新規性の高いいくつかの発見を行っており、その現象の解析についても詳しい議論がなされている。また、波長可変な超短パルスを得るための光学パラメトリック増幅器を自作するなど装置面での創意工夫が成されている。従って、そのオリジナリティは高く、博士論文として十分な質を備えたものと判断した。なお、口述試験において申請者に対して審査委員から研究目的、方法論、得られた結果に関する質問がされたが、的確な回答があり、その知識は博士(理学)に値するものだと認められた。論文は平易な英語が書かれており、英語力に関しても十分なものと判断した。また、公開発表会においても質疑応答に対して的確な応答を行い、申請者は博士(理学)に相応しいと判断した。