

Probing of an Adsorbate-Specific Excited State on an Organic Insulating Surface by Two-Photon Photoemission Spectroscopy

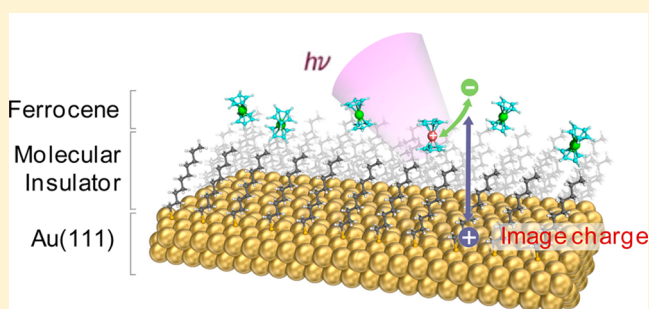
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S Supporting Information

ABSTRACT: In this study, we investigate the photoexcited electronic states of ferrocene (Fc) molecules adsorbed on an organic insulating surface by two-photon photoemission spectroscopy. This insulating layer, composed of a decanethiolate self-assembled monolayer formed on an Au(111) substrate, enables us to probe the electronically excited states localized at the adsorbed Fc molecules. The adsorbate-specific state is resonantly excited by photons at 4.57 eV, which is 0.5 eV smaller than the energy of the first molecular Rydberg state of free Fc in the gas phase. This result indicates that the electrons are bound to both the excited hole formed in the adsorbate and the positive image charge induced in the substrate. The hybridized electronic characteristics of the adsorbate-specific state are responsible for the strong transition selectivity and short lifetime of the excited state.



1. INTRODUCTION

The properties of electronically excited states have attracted increasing interest in fields ranging from spectroscopy to photochemistry and biology.^{1,2} The temporal dynamics of excited states are particularly important because many photochemical and photophysical properties of organic molecules depend on the kinetics of excited-state processes following the absorption of photons. The excited states of organic molecules are generally quite sensitive to their environments. For example, when organic molecules are adsorbed on metal surfaces, their molecular properties are affected by electronic interactions with the substrate, which may modify the functional properties of the molecules from those of liquid and gas phases. A number of researchers have exploited these phenomena to tune molecule–substrate interactions.^{3–11} Molecules adsorbed on surfaces of wide band gap solids are especially promising for this purpose, where a local electronic structure with specific molecular functionality should decouple from delocalized electronic structures on the substrate. The fabrication of thin insulating films on a metal substrate has been frequently reported with spacer layers of oxides,^{4,5} alkali halide,^{7,8} nitride,⁹ rare gases,¹² and molecules.⁶ As an insulating spacer layer, the self-assembled monolayer (SAM) is gaining popularity because it can be easily prepared, its insulating function can be easily designed, and its functional units can be miniaturized.^{6,13–17}

Recently, we reported that an alkanethiolate-SAM formed on an Au(111) substrate is an excellent insulator in which excited

electrons persist for a lengthy period in the image potential state (IPS).¹⁸ As such, SAM substrates are expected to support organic molecules without disturbing their native properties. In this study, we investigate the versatility of a SAM as a supporting substrate by depositing ferrocene molecules, $\text{Fe}(\text{C}_5\text{H}_5)_2$ (Fc), on the surface of 1-decanethiolate ($\text{C}_{10}\text{H}_{21}\text{S}$)-SAM. The alkyl moiety of this SAM has a large energy gap of ~ 9 eV.¹⁹ Fc is a model compound for investigating organometallic systems owing to its high molecular symmetry²⁰ and its stable closed “18-electron” shell configuration.²¹ The physical and chemical properties of Fc have been extensively studied by optical spectroscopy including laser spectroscopy in gas and solution phases^{22–29} and photoelectron spectroscopy in the gas phase^{30,31} and adsorbed systems.^{32,33} Here, we have investigated electronic structures including excited metastable states of Fc adsorbed on the SAM by two-photon photoemission (2PPE) spectroscopy and ultraviolet photoelectron spectroscopy (UPS). 2PPE is a powerful experimental tool for probing electronic structures below and above Fermi level (E_F) and transient excited states at the surface.^{34,35} In 2PPE, an electron in an occupied state is excited into an unoccupied state by a first photon, where it is probed by a second photon. Furthermore, the dynamics of the excited electrons can be investigated by a pump–probe method with femtosecond (fs) time resolution. By using these

Received: August 27, 2013

Published: January 22, 2014

techniques, we identified not only the unperturbed molecular orbital but also the molecular excited state specific to the surface adsorbate, which is not formed in free molecules.

2. EXPERIMENTAL SECTION

2.1. Two-Photon Photoemission. All 2PPE experiments were performed in an ultrahigh vacuum (UHV) chamber at a base pressure lower than 8×10^{-9} Pa. In the single-color 2PPE experiment, one photon promotes the electron to the intermediate state, and a simultaneously coming second photon of equal energy releases the electron for detection. This experiment adopted the third harmonics (photon energy, $h\nu = 4.04\text{--}4.89$ eV) of a tunable Ti:Sa laser (COHERENT: Mira-900F, 76 MHz, 100 fs, 780–920 nm) as a photon source. In the two-color 2PPE measurements, the third harmonics were employed as pump photons, while the probe photon is the partially separated fundamental or its second harmonics. The optical delay between the pump and probe photons was controlled by a precision stage with a minimum step of 100 nm, corresponding to 0.67 fs per step. The lights were focused by a concave mirror onto the sample surface in the UHV chamber at an incident angle of 55° . Apart from polarization dependence, all measurements were performed using the *p*-polarized pump and probe photons. The probe area was limited to the spot size of the third harmonics on the sample ($\phi < 0.1$ mm). To protect the organic sample from radiation damage, the incident laser power was reduced by maintaining the power of the ultraviolet third harmonics to below 0.13 nJ/pulse. Photoelectrons emitted normal to the surface (except for the angle-resolved 2PPE) via two-photon processes were detected by a hemispherical electron energy analyzer (VG: Alpha110). The resolutions of total energy and time in the 2PPE setup were ~ 20 meV and 30 fs, respectively. By replacing the light source with a He–I discharge lamp ($h\nu = 21.22$ eV), the same apparatus enabled UPS. The sample temperature was retained at 90 K during all photoemission experiments.

2.2. Sample Preparation. An Au(111) single crystal ($d = 10$ mm, $t = 1$ mm, MaTech GmbH) was cleaned by repeated cycles of Ar⁺ ion sputtering (0.6 kV, ~ 1 μ A, 15 min) and annealing (770 K, 30 min) in the UHV chamber. 2PPE measurement yielded a work function of 5.5 eV and a sharp Shockley surface state at 0.4 eV below E_F , confirming the cleanliness of the surface.³⁶ To create the SAM film, the Au(111) substrate was immersed in a 1-decanethiol ($C_{10}H_{21}SH$) ethanolic solution (~ 0.1 mM) for 20 h. The sample was rinsed in pure ethanol and then immediately introduced to the UHV chamber through the load lock. The geometric structure of the SAM film was checked by scanning tunneling microscopy (STM) with molecular resolution, which has been reported in a separate paper.³⁷ The STM study has revealed that the SAM film has the molecularly ordered “standing-up” structures with $\sqrt{3} \times \sqrt{3}$ -R30° or $c(4\sqrt{3} \times 2\sqrt{3})$ -R30° periodicity with an average domain size of ~ 20 nm. Fc (99%, Sigma-Aldrich) was deposited on the SAM film by exposing the sample to molecular vapor at 90 K. Molecular coverage was controlled by the exposure time and was estimated from the change in work function from a preliminary calibration experiment.

3. RESULTS AND DISCUSSION

3.1. Occupied Electronic Structure of Fc-Adsorbed SAM. Figure 1 shows UPS spectra of the SAM deposited with varying amounts of Fc (0–2.2 monolayer (ML)). The intensity of each spectrum was normalized by the binding energy of 5 eV, at which no significant changes were induced by Fc deposition. The shoulder-like feature at $E_F - 2.6$ eV has been previously assigned to the Au-derived signal.³⁶ Following Fc deposition on the SAM, new occupied electronic structures, H1 and H2, appeared at 1.9 and 4 eV below E_F , respectively. These structures are clarified in the difference spectra (inset of Figure 1) obtained by subtracting the spectrum of the bare SAM from each spectrum of the Fc-deposited SAM. The intensities of both H1 and H2 monotonically increased and nudged toward

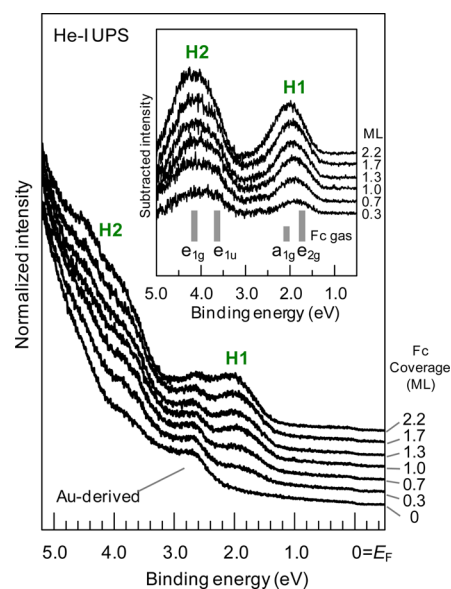


Figure 1. Dependence of He–I UPS spectra on Fc coverage on SAM. Fc-derived signals, H1 and H2, appeared after Fc deposition. (Inset) Difference between deposited Fc and bare UPS spectra. The UPS data of the gas-phase Fc from ref 31 are also indicated.

higher binding energy (>1 ML) as Fc coverage increased. On the basis of theoretical calculations of the ground-state molecular orbitals and experimental studies of gas-phase photoemission by Fc molecules,^{30,31,38} the observed photoemission features were assigned to the molecular orbitals of Fc; the highest occupied molecular orbital (HOMO) (e_{2g}) and the next HOMO (HOMO-1) (a_{1g}) correspond to H1, while H2 is attributable to the deeper molecular orbitals of HOMO-2 (e_{1u}) and HOMO-3 (e_{1g}). The inset of Figure 1 also shows the energy level of each orbital obtained by gas-phase UPS.³¹ The energy positions of e_{2g} and a_{1g} were consistently aligned to those of H1, whereas e_{1u} and e_{1g} aligned with H2.

3.2. Unoccupied Electronic Structures of Fc-Adsorbed SAM. Figure 2 shows the 2PPE spectra of the SAM deposited with varying amounts of Fc. The photon energy was set to 4.54 eV. The horizontal axis indicates the intermediate energy with respect to E_F , representing the energy of electrons excited by the pump photon in the 2PPE process. A weak spectral feature, labeled C in the spectrum of the bare SAM, was assigned to an unoccupied state derived from the Au–S bond located at 3.7 eV above E_F .^{36,39} Details of the electronic structure, including C in alkanethiolate-SAMs of various chain lengths, are given in refs 36 and 39. When Fc is deposited, a noticeable feature, labeled A*, appears at $E_F + 2.6$ eV, where A* denotes an adsorbate-specific excited state (Section 3.3). The intensity of A* increased in low Fc coverage but was saturated at ~ 0.7 ML. At higher coverage (>2 ML), the A* peak was broadened and was shifted slightly toward lower energy. The inset in Figure 2 shows the spectra of the 0.3 ML Fc/SAM by changing the detection angles of photoemission (θ) with respect to the surface normal. We note that the energy of A* is nearly independent of θ , indicating that A* has little band dispersion parallel to the surface.

However, the spectral form of A* strongly depends on the photon energy. Figure 3 demonstrates the dependency of the 2PPE spectra of the 0.3 ML Fc/SAM on photon energy. All spectra were aligned along the intermediate energy. Because the intermediate energy of A* is independent of $h\nu$, it can be

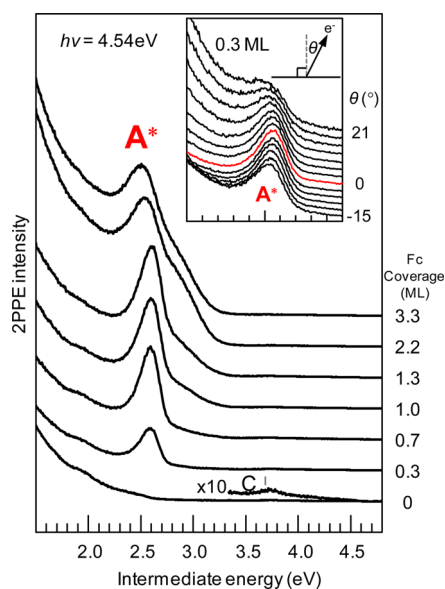


Figure 2. 2PPE spectra for 0–3.3 ML coverage of Fc on SAM at $h\nu = 4.54$ eV. The horizontal axis indicates the intermediate energy with respect to E_F . Inset shows how A^* at 0.3 ML depends on photoemission detection angles. The energy band dispersion of A^* is scarcely discernible.

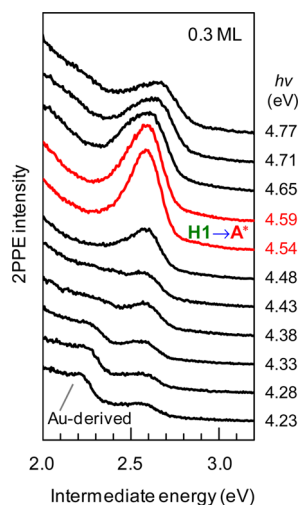


Figure 3. Photon energy dependence of 2PPE spectra of 0.3 ML Fc. Corresponding $h\nu$ s are listed along the right vertical edge.

assigned to an unoccupied state or to some excited states. It should be noted that the intensity of A^* was significantly enhanced at photon energies of 4.54 and 4.59 eV, indicating that resonance excitation to A^* occurs from a specific occupied state whose energy difference matches these photon energies. The energy position of the initial state is estimated at 1.97 eV below E_F , which is consistent with the H1 peak in the UPS (Figure 1).

An unoccupied IPS, which is generated by a two-dimensional (2D) potential well formed by the Coulomb-like attractive image potential barrier and the repulsive surface barrier, can be observed by time-resolved 2PPE at considerable time delays. Figure 4 shows the 2PPE spectra of the bare SAM (bottom) and SAM deposited with 0.3 ML Fc (upper) at delay times (Δt) of zero (dotted lines) and 800 fs (solid lines) between the pump and probe photons. The photon energies of pump

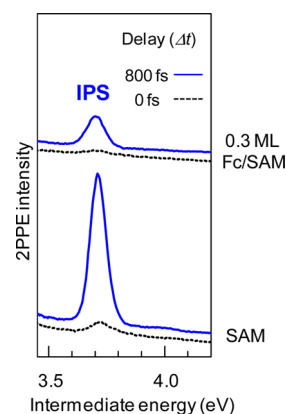


Figure 4. 2PPE spectra of 0 ML (lower) and 0.3 ML (upper) Fc, collected at $\Delta t = 0$ fs (dotted line) and $\Delta t = 800$ fs (solid line). The photon energies were $h\nu_{\text{pump}} = 4.33$ eV and $h\nu_{\text{probe}} = 1.44$ eV. The pump and probe laser powers were fixed at 0.013 and 1 nJ/pulse, respectively.

($h\nu_{\text{pump}}$) and probe ($h\nu_{\text{probe}}$) photons were 4.33 and 1.44 eV, respectively. The laser powers were retained constantly throughout the measurements. Although the energy of IPS accidentally coincides with that of C ($E_F + 3.7$ eV) at 90 K, both states are distinguishable by their temperature dependences; the energy of C shifts toward E_F as the sample temperature increases.³⁶ At 0.3 ML coverage (upper plots in Figure 4), the IPS intensity was rather attenuated but remained clearly visible. The energies of the electronic states determined by UPS and 2PPE are summarized in Figure 5.^{24,26,31,40}

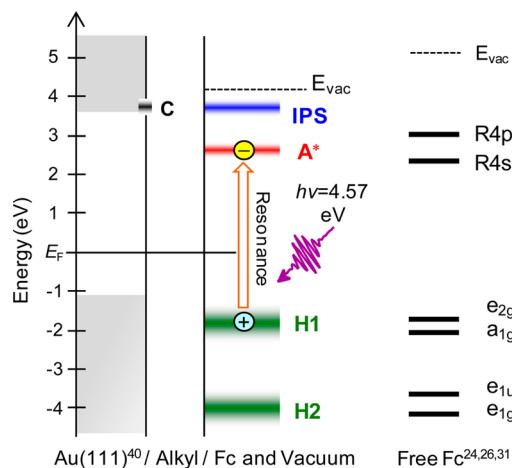


Figure 5. Schematic of observed energy levels in 0.3 ML Fc on SAM. The projected band of Au(111) at the Γ point was extracted from ref 40. The electron–hole pair is created by resonant excitation at the corresponding photon energy. Occupied³¹ and unoccupied levels^{24,26} of gas-phase Fc aligned to H1 are indicated in the right.

Figure 6a,b shows the time evolution of IPS and A^* for the 0.3 ML Fc/SAM, which was obtained from time-resolved 2PPE measurements. Electron excitations to IPS and A^* were generated at $h\nu_{\text{pump}} = 4.54$ eV, $h\nu_{\text{probe}} = 3.02$ eV and $h\nu_{\text{pump}} = 4.33$ eV, $h\nu_{\text{probe}} = 1.44$ eV, respectively. Although the lower $h\nu_{\text{probe}}$ provides a better signal-to-noise ratio, A^* at $E_F + 2.6$ eV must be detected at a higher $h\nu_{\text{probe}}$ to overcome the workfunction of 4.2 eV in this system. The IPS survived over several picoseconds, whereas A^* significantly attenuated within

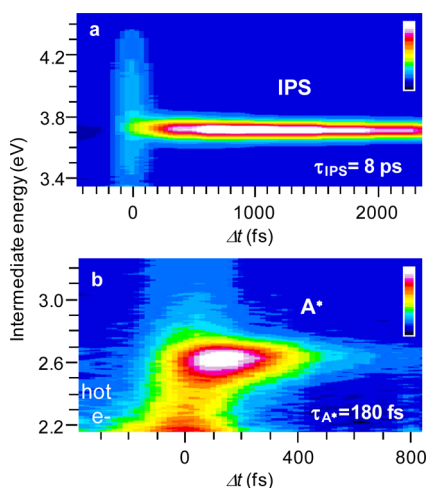


Figure 6. 2PPE spectra of 0.3 ML at (a) IPS and (b) A* regions with varying Δt . The photon energies applied to the A* and IPS regions are $h\nu_{\text{pump}} = 4.54$ eV, $h\nu_{\text{probe}} = 3.02$ eV and $h\nu_{\text{pump}} = 4.33$ eV, $h\nu_{\text{probe}} = 1.44$ eV, respectively. The background spectrum (without irradiating probe photons) was subtracted from each spectrum. Energies of IPS and A* were nearly independent of Δt . The evaluated lifetimes of IPS and A* were $\tau_{\text{IPS}} = 8$ ps and $\tau_{\text{A}^*} = 180$ fs, respectively.

1 ps. The lifetimes of the excited electrons in the IPS (τ_{IPS}) and A* (τ_{A^*}) were evaluated as 8 ps and 180 fs, respectively. Within the lifetimes of both states, no significant shift in the peak positions, such as measurable energy relaxation, occurred. The tailing at the negative delay near $E_{\text{F}} + 2.2$ eV arose from hot electrons excited by $h\nu_{\text{probe}}$.⁴¹

In addition, A* and IPS showed strong polarization dependence of the probe photon, as shown in Figure 7. The geometric configuration of incident light and its polarizations are displayed at the top left in the figure. Each polarization-dependent spectrum was obtained at its maximum intensity with an appropriate time delay of $\Delta t = 140$ fs for A* and $\Delta t = 1$ ps for IPS. As expected from its physical origin, IPS was clearly selective for the polarization of probe photons. Interestingly, A* was similarly detected by only *p*-polarized probe photons, implying that the transition moment of its photoemission is perpendicular to the surface.

As shown in Figure 6, the lifetime of IPS formed on the 0.3 ML Fc/SAM was exceptionally long (8 ps) and close to that of the bare SAM (11 ps).⁴² According to recent reports, the intensity and lifetime of IPS are quite sensitive to molecular ordering; when ferrocenyl alkanethiolate molecules are introduced to the SAM, the alkyl chain ordering is largely disordered, reducing the IPS lifetime to ~ 1 ps.⁴² The long IPS lifetime in the present Fc/SAM system indicates that the SAM is not disordered by Fc adsorption. In addition, the occupied orbitals H1 and H2 derived from Fc molecules were verified by UPS, as discussed in Section 3.1. These results suggest that Fc molecules are adsorbed on the SAM without molecular dissociation, although Fc is fragmented on the Au(111) surface by strong chemical interactions.⁴³ Our infrared reflection absorption spectroscopy (IRAS) measurements also indicate that Fc molecules are molecularly adsorbed on the SAM surface in a random orientation without penetrating into the film and desorb from the surface at a rather low temperature (~ 200 K), whereas the ordering of the SAM is not affected by depositing Fc, as described in the Supporting Information. On the basis of these experimental findings, we conclude that Fc molecules

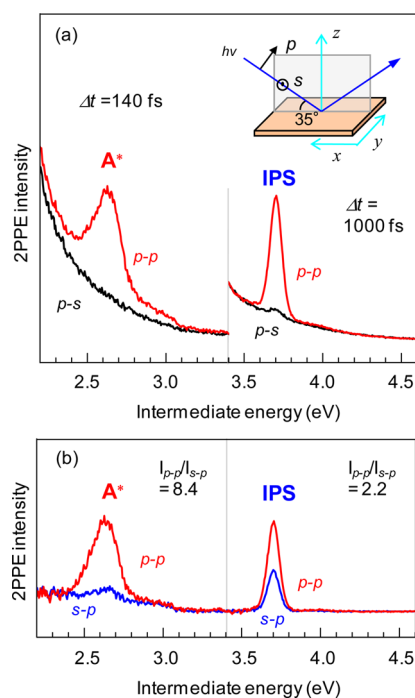


Figure 7. (a) Influence of probe photon polarization on the 2PPE signal of 0.3 ML Fc/SAM with *p*-polarized pump photon. The upper right part of the figure shows the experimental geometry. (b) Dependence of the pump photon with a fixed *p*-polarized probe photon in which the backgrounds taken with the *s*-polarized probe photons were subtracted from each spectrum. Photon energies were identical to those of Figure 6. Δt s of the A* and IPS regions were 140 and 1000 fs, respectively, where the intensity of each signal was near maximal.

gently adsorb on the SAM without disturbing the molecular ordering of the film. In addition, as shown in Figure 1, the energies of H1 and H2 were nearly constant up to 1 ML, suggesting that the adsorbed molecules do not interact with each other; that is, the Fc molecules are dispersedly adsorbed on the SAM surface. This inference is supported by the relationship between coverage and IPS intensity. Reportedly, the surface coverage of the clean substrate area can be monitored by IPS.⁴⁴ In the present system, the IPS intensity is attenuated to $\sim 25\%$ at a mere 0.3 ML coverage of Fc. This result suggests that Fc molecules deposited at low coverage (< 1 ML) do not aggregate into island-like structures but instead disperse across the SAM surface. If the reverse was true, the IPS intensity would approach 70% of that of the clean substrate.

3.3. Characterization of A* State. Upon first consideration, the A* state appears to be the lowest unoccupied molecular orbital (LUMO) (e_{1g}^*) or the next LUMO (LUMO + 1) (e_{2g}^*) of Fc.^{23,30,45} However, this possibility is excluded by the dependence of A* intensity on coverage. Although the photoemission intensity derived from molecular orbitals generally increased with molecular surface density, at least up to a few ML, the A* intensity saturated at only 0.7 ML (Figure 2). Indeed, as revealed in the UPS spectra in Figure 1, the intensities of the molecular-derived occupied H1 (e_{2g} and a_{1g}) and H2 (e_{1u} and e_{1g}) states monotonically increased with Fc coverage, up to 2.2 ML. Thus, the A* state cannot arise from a simple LUMO (e_{1g}^*) of Fc.

Alternatively, A* may signify an excited state induced by electrons bound near the surface. Because the A* signal is

detected only by *p*-polarized probe photons (Figure 7), the transition dipole moment from A^* to the final free electron state is directed normal to the surface in a manner similar to that of IPS. In contrast to IPS, however, the A^* state showed little energy dispersion, indicating that electrons excited to A^* are localized on the surface (Figure 2 inset). In addition, since the spectral form depends on photon energy (Figure 3), resonance excitation to A^* can occur from H1, where a photoexcited hole is created at H1 in the Fc molecule. From these experimental findings of polarization dependence, band dispersion, and resonant excitation, we conclude that the A^* state likely originates from an adsorbate-specific excited state in which the excited electron is bound to both the excited hole created in the Fc molecule and to the positive image charge induced in the substrate.

In free molecules in the gas phase, excited states bound to ionic cores have been observed as Rydberg states.^{24–26,28,29} The gas-phase UV absorption spectrum of Fc clearly reveals that electronic transition from the nonbonding iron 3d (a_{1g}) orbital to the molecular Rydberg 4p (e_{1u}) orbital occurs at an excitation energy of 5.1 eV.^{24–26,28,29} In our study of Fc molecules adsorbed on the SAM, excitation from H1 to A^* at 4.57 ((4.54–4.59)/2) eV, shown in Figure 3, seems to correspond to excitation from 3d to Rydberg 4p (5.1 eV in free Fc molecules), where the excitation energy is lowered by induced image charges in the substrate. According to the above scenario, it can be considered that the potential for electrons in the adsorbate-specific excited state is composed of two contributions including image potential and attraction by the positive hole. As is well-known, the energy of the lowest IPS is ≤ 0.85 eV below the vacuum level (E_{vac}).³⁵ In our study, the lowest IPS formed on the SAM was 0.5 eV below E_{vac} , as summarized in Figure 5. Therefore, it seems reasonable that the excitation energy of the adsorbate-specific A^* state is 0.5 eV lower than that of the Rydberg state in free Fc, owing to the contribution of the image potential. Although excitation from 3d to Rydberg 4s state is not allowed in the gas phase, there is a possibility that A^* originate from Rydberg 4s, where the energy is 0.25–1.1 eV lower than that of 4p,^{24,26} because the symmetry of the molecular orbital may be modified on the surface. However, it can be considered that the molecular orbital symmetry for the gas-phase Fc is nearly conserved for the adsorbed Fc because the interaction between the Fc and alkanethiol molecules in the SAM seems to be very weak. In fact, such weak interaction was verified by our IRAS measurements, which showed that Fc has a random orientation on the SAM and easily desorbs from the SAM surface at ~ 200 K (Supporting Information). By considering the contribution of image potential to stabilize the excited electrons, it seems reasonable to attribute A^* to the modified Rydberg 4p state rather than to the 4s state.

The polarization dependence of 2PPE yields offers a key to the understanding of the electron excitation mechanism in the 2PPE process. Because the A^* state can be essentially regarded as a hybridized excited state of the IPS and the Rydberg state, it demonstrates the characteristics of both states and would show strong polarization selectivity on the probe pulse, as shown in Figure 7a. That is, the A^* state behaves as an adsorbate-specific excited state, in which electrons are bound by both holes localized on the adsorbed molecules and by image charges induced in the substrate. Although both A^* and IPS can be observed by only *p*-polarized probe pulse, A^* shows stronger dependence on the polarization of pump pulse than IPS, as

shown in Figure 7b. From the detailed analysis of their polarization dependence (Supporting Information), it is concluded that the IPS electron is supplied from the metal substrate of Au(111), whereas that of A^* is photoexcited directly from the occupied orbital in the adsorbed Fc molecule.

Next, we discuss how the A^* state differs from a charge-transfer exciton (CTE).^{46,47} In organic semiconductors, light absorption creates correlated electron–hole pairs known as excitons, which are strongly bound and localized to one or a few lattice sites (Frenkel excitons). Furthermore, in organic–organic semiconductor interfaces composed of electron donors–acceptors (D/A) with low dielectric constants, charge separation at the D/A interface creates bound electron–hole pairs across the interface known as CTEs.^{46,47} Zhu and co-workers reported similar CTE formation at organic semiconductor surfaces,^{48–50} in which excited electrons are transiently bound by the Coulomb potential from holes as well as by the polarization of the organic semiconductor. If Fc molecules form a well-ordered crystalline film, A^* will grow up into CTE. On the SAM, however, because Fc molecules are adsorbed with random orientations, as indicated by the IRAS measurement, the Fc film would have a poor ordering and would not generate a clear CTE state. In fact, at a higher Fc coverage, A^* becomes broader and shifts toward higher binding energy, as shown in Figure 2, which suggests that A^* would be quenched by the aggregation of Fc molecules to result in the maximum intensity around 0.7 ML. In CTEs, since holes are created inside the dielectric layers, the binding energy between an excited electron and its corresponding hole is suppressed by the screening effect of surrounding dielectric materials. In contrast to the holes in CTE, the holes in this study are localized on Fc molecules adsorbed to the SAM film. Thus, the A^* state is not subject to organic layer screening. This lack of the screening effect may render the A^* state (1.1 eV) more stable than that of CTE, which is ~ 0.5 eV relative to IPS.⁵⁰ To evaluate the validity of the proposed mechanism, simple calculation based on the 1D dielectric continuum model (DCM),^{51,52} which is often used to calculate the IPS forming on the dielectric materials, has been performed; details are described in the Supporting Information. The result approximately supports the present model, although more systematic experiments and theoretical investigation expanding to a 3D calculation should be conducted for the quantitative discussion, particularly on the adsorption geometry of Fc.⁵³

Large lifetime difference between IPS ($\tau_{IPS} = 8$ ps) and A^* ($\tau_{A^*} = 180$ fs) can be reasonably explained by their characteristics; the electrons excited to IPS are well separated from the metal substrate and follow no relaxation path owing to the excellent insulating property of SAMs. On the other hand, electrons excited to A^* can decay by recombining with adjacent holes in the adsorbate or by relaxing into the lower excited states. Interestingly, the lifetime of the excited Rydberg 4p state in gas-phase Fc (excitation energy = 5.1 eV) has been reported to be 200 fs,²⁷ which is comparable to that of A^* . In the gas phase, molecular excitons typically have characteristic lifetimes on the order of nano to picoseconds.⁵⁴ Therefore, the short lifetime of A^* (180 fs) should be interpreted by the rapid relaxation to the other excited state in lower energy, which also supports the fact that A^* is originated from a higher excited state such as Rydberg 4p. The lower excited state, most likely Rydberg 4s, could not be observed in the present experiments likely because of the limited energy window or the off-resonance condition. Note that no higher quantum states were

detected at energies between A* and IPS, although these states are expected. In our experiment, the pump photon energy was limited to 4.77 eV, which is insufficient for exciting the electrons from H1 to higher quantum states.

4. CONCLUSIONS

Through 2PPE spectroscopy of the Fc/SAM system, we demonstrated that photoinduced excited states are formed in molecules adsorbed on the insulating surface. The energy of the adsorbate-specific excited state was lower than that of the Rydberg state of free molecules or IPS on the bare surface because the excited electrons are bound by both excited holes created in the adsorbed molecules and a positive image charge induced in the substrate. These conditions should typify adsorbed molecules that are electronically well separated from the metallic substrate and are largely responsible for the chemical surface reactions occurring in these systems.

■ ASSOCIATED CONTENT

Supporting Information

IRAS analysis of the Fc/SAM system, supplemental discussion of Figure 7b, and numerical calculation for A*. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Prof. T. Munakata and Dr. T. Yamada of Osaka University for providing DCM computer code and for fruitful discussion. This work is partly supported by MEXT-Supported Program for the Strategic Research Foundation at Private Universities, 2009-2013, and by MEXT-Grant-in-Aid for Young Scientists (B) (no. 25810010).

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