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Description	

Optical Second Harmonic Generation Phase Measurement at Interfaces of Some Organic Layers with Indium Tin Oxide

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Abstract :

We observed phase shift in optical second harmonic generation (SHG) from interfaces of indium tin oxide (ITO)/copper phthalocyanine (CuPc) and ITO/pentacene. Phase correction due to Fresnel factors of the sample was taken into account. The phase of SHG electric field at the ITO/pentacene interface, $\phi_{interface}$ with respect to the phase of SHG of bare substrate ITO was 160°, while the interface of ITO/CuPc had a phase of 140°.

Keywords :

Second harmonic generation, Phase measurement, Indium tin oxide, Organic semiconductor, Interface dipoles, Charge transfer

1. Introduction

Organic-based devices are economically advantangeous and their application to flexible electronics are also very attractive. In the operation of organic devices, the role of interfaces are important [1-2]. Electron probes such as ultraviolet photoelectron spectroscopy (UPS), X-ray photoemission spectroscopy (XPS), inverse-photoelectron spectroscopy(I-PS) or low energy electron diffraction (LEED) methods can not generally access interfaces with considerable front thickness [1-6]. Here the approach of non-linear optics is becoming powerful in investigating such buried interfaces [7-10]. Several groups have characterized organic light emitting diodes (OLEDs) by using second harmonic generation (SHG) [11-12] and sum frequency generation (SFG) [13]. The information on local electric field and carrier distribution in the organic devices were obtained. In the latest trend, the use of doubly-resonant SFG has also been explored as a nondestructive vibrational spectroscopic probe of buried organic layer in OLED [14]. Characterization of OLED devices must be strictly depth selective since these devices have complicated layer and interface structures.

Matsushima et al reported an improvement of electrical properties of indium tin oxide (ITO)/N-N'-diphenyl-N-N'-bis(1-naphthly)-1,1'-biphenyl-4,4'-diamine (α-NPD) interface by inserting a dielectric layer of molybdenum trioxide (MoO_3) between the α-NPD and ITO layers [15-16]. Strong response from permanent dipoles at the interface MoO_3/α-NPD was later observed via SHG measurement by El-Basaty et al [11]. In their analysis of second order nonlinear susceptibility, $\chi^{(2)}$, they suggested that the permanent dipoles at this α-NPD/MoO_3 interface has the opposite sign to the dipoles at MoO_3/ITO. Here they used an observation by Lalama and Garito [17] that the nonlinear susceptibility has generally the same sign as that of the permanent dipole.

However, more generally speaking, the two $\chi^{(2)}$'s at ITO/MoO_3 and MoO_3/α-NPD may not have exactly 180° phase difference. This is because $\chi^{(2)}$ here is a complex quantity and its phase difference may deviate from π [18-19]. Phase shift of $\chi^{(2)}$ at the interface of organic layer induced by fluctuation of the interface dipoles is also possible [20]. Hence, it is favorable if we can measure the phase relation between the two $\chi^{(2)}$'s in order to find out more about the static dipoles at the interfaces. Now, in order to check the phase information from interface dipoles, the homodyne measurement used by El-Basaty et al alone is not enough. We will need to use a method called "heterodyne measurement" utilized by Kemnitz et al [21]. In this method, a second reference source of SHG is inserted into the output path of the beam in order to produce an interference pattern between the SHGs from the sample and the reference, as the reference source is moved along the optical path [21-24].

In this paper, our purpose is to demonstrate the phase measurement of SHG originating from the organic layer interface. The SHG phase measurement has been used in investigations of both organic [7, 21-26] and inorganic [8, 18-19, 22] materials. The phase measurement is very convenient to check the molecular orientation of organic adsorbates on the surface or interface [9]. However, the phase measurement from the buried interface of organic semiconductor has never been reported. Since our interface is buried under the organic thin film, the analysis of dielectric dispersion of the film should be properly considered. Other than the experiment of the SHG phase, relative SHG intensities and SHG spectra should also be measured separately.

Our samples consisted of a double layered system of ITO and organic semiconductor. We selected pentacene and copper phthalocyanine (CuPc) as organic materials in this paper. Pentacene and CuPc are known to assist hole injection at the ITO interface because of the relations between their energy levels as follows. Ionization potential energy, I_p is the molecular equivalent of the work function [27]. In our context, it is defined as the energy difference between the highest occupied molecular orbital (HOMO) energy level and the vacuum level. In the measurement of AC-2 photoelectron spectroscopy (Riken Keiki), the ionization energies, I_p of pentacene and CuPc at the interface of ITO are 4.84 ± 0.02 eV and 4.98 ± 0.02 eV, respectively. The work function of the substrate ITO was determined to be 5.02 ± 0.02 eV [28]. Pentacene and CuPc are reported to be well-oriented on the ITO surface [6, 29-30], and they are commonly used organic materials. Although the study of interface of ITO/CuPc has implied the presence of interface states, the property of the interface has not been discussed extensively [6]. Since the energy difference of ITO/pentacene is larger than that of ITO/CuPc, the electronic potential at the interface of the former is inferred to be stronger.

2. Experimental

For sample preparation, the ITO substrates of thickness 150 nm were ultrasonically cleaned with acetone, detergent, pure water, and isopropanol. Then, the substrates were treated in UV-ozone. The organic thin films of thickness 100 nm was vacuum-deposited on the ITO substrates. The sample was then glass capped in dry N_2.

The optical measurement set-up was mostly the same as that reported in Ref. 11. Figure 1 shows the optical scheme near the sample in our SHG phase measurement. The fundamental light of photon energy, ħω at 1.17 eV from a Nd:YAG laser system irradiated the sample at the incident angle of ~45°. The pulse energy reaching the sample was ~ 40 μJ. In the output path, the frequency doubled 2ω light was separated from the fundamental one by using ω cut filters (Sigma Koki, SCF-50S-580) and a monochromator. The 2ω light was detected by a photomultiplier and the electric signal was gated and amplified with a boxcar integrator and was accumulated in a personal computer.

The method of using SHG interference to obtain molecular directionality from the buried interface was introduced by Kemnitz et al in 1986 [21]. We adopted a similar optical configuration. The phase shifting unit (PSU), α-SiO_2 (0001) crystal on a moving stage was inserted in the output beam path [31]. The intensities of the overlapping SHG from the sample and the PSU crystal were plotted as a function of the moving distance of the PSU. SHG from a bare substrate ITO of 150 nm thickness was observed in a similar way. The polarization combination was 45°-in/p-out as a first example to check the phase of SHG from the interface. More specific polarization combination is required to interpret the effective $\chi^{(2)}$ elements from the interface. In this phase measurement, ITO behaves as a reference to probe the buried interface contributions [10, 18-19, 23-24, 31]. Therefore, the SHG signal of the ITO/organic interfaces can be separated from that of an SHG active substrate. Similar measurement was made in systems such as self-assembled monolayers (SAMs) adsorbed on SHG active metal surfaces [32].

The phase difference between the SHG signal generated from the sample ITO/organic interface and the reference α-SiO$_2$ (0001) is given as $\phi_{ITO/organic}$,

$$\phi_{ITO/organic} = \frac{2\pi}{\lambda_{2\omega}} \left[\left(n_{2\omega}^{air} - n_{\omega}^{air}\right)s + \left(n_{2\omega}^{organic} - n_{\omega}^{organic}\right)d\right] + \phi_{ITO/organic,0}. \quad (1)$$

Here the difference of the refractive indices of air under standard air condition is $\left(n_{2\omega}^{air} - n_{\omega}^{air}\right) = 4.22\ x\ 10^{-6}$ [33], the SHG wavelength is $\lambda_{2\omega} = 532$ nm (2.33 eV in photon energy) and the organic thin film thickness is $d = 100$ nm. Parameter s is the distance between the moving α-SiO$_2$ (0001) and the sample's surface, while $\phi_{ITO/organic,0}$ is the phase of $E_{ITO}^{(2\omega)} + E_{interface}^{(2\omega)}$ at the ITO/organic interface. $E_{ITO}^{(2\omega)}$ and $E_{interface}^{(2\omega)}$ are the SHG electric field from ITO and the ITO/organic interface, respectively. The phase $\phi_{ITO/organic}$ will be modified by optical dispersion of the organic layer as given by the second term in Eq. (1). We also define the phases of the SHG from the sample ITO as ϕ_{ITO} and $\phi_{ITO,0}$ in the same way.

The total SHG is the superposition of the SHG from the sample and the PSU crystal as [26]

$$I_{total} \propto \left|E_{ITO}^{(2\omega)} + E_{interface}^{(2\omega)} + E_{a-SiO2}^{(2\omega)}\right|^2. \quad (2)$$

In our technique, we employed an α-SiO$_2$ crystal with SHG intensity of 10 times that of the organic sample [24, 34]. The electric field at 2ω from the ITO/organic sample is $E_{sample}^{(2\omega)} = E_{ITO}^{(2\omega)} + E_{interface}^{(2\omega)}$. Here $E_{ITO}^{(2\omega)}$ emerges from the ITO substrate. Hence, the total SHG intensity, I_{total} is derived as the sum of the two SHG sources [29].

$$I_{total} = I_{sample} + I_{\alpha-\mathrm{SiO2}} + 2\sqrt{I_{sample}\, I_{\alpha-\mathrm{SiO2}}}\ \cos \phi_{ITO/organic}, \qquad (3)$$

The periodicity of the SHG interference pattern as the PSU is translated in air is determined from Eq. (1) as

$$l_o = \frac{\lambda_{2\omega}}{n_{2\omega}^{air} - n_{\omega}^{air}}\ . \qquad (4)$$

The periodicity, l_o is calculated as 126 mm.

3. Result

3.1 SHG Phase $\phi_{ITO/organic}$ and SHG Spectra of ITO/organic Interfaces

Figure 2 shows the SHG intensity of ITO, ITO/CuPc and ITO/pentacene as a function of the PSU crystal translation distance s in the output line. As can been seen, they are fitted very well by cosine functions as:

$$f(s) = y_o + A\, cos\,(fs + \alpha\,). \qquad (5)$$

At least one period of oscillation of SHG intensity is seen in each measurement. Thus, the phase information from this SHG interference pattern can be extracted from the parameters given by the fitted cosine function. The frequency of SHG in air at periodicity of 126 mm is calculated as 49.87 x 10^{-3} mm^{-1}. Relative comparison shows that all measured spatial frequencies are within the range of 0.04987 ± 0.006 mm^{-1}. This indicates small error in the measurement.

Equation (5) can be compared with Eq. (3). The value $(fs + \alpha)$ in Eq. (5) can be interpreted as $\phi_{ITO/organic}$ in Eq. (3). From Eq. (1), the parameter of $\frac{2\pi}{\lambda_{2\omega}}(n_{2\omega}^{air} - n_{\omega}^{air})$ can substitute the frequency *f*, while $\frac{2\pi}{\lambda_{2\omega}}\left(n_{2\omega}^{organic} - n_{\omega}^{organic}\right)d + \phi_{ITO/organic,0}$ is equal to the phase, α. We note here that relatively negligible SHG could be detected from separate thin films of CuPc and pentacene. So, there is effectively no contribution from the bulk SHG from the organic thin films.

Figure 3 shows SHG spectra of the three samples. The dashed line indicates the SHG photon energy of 2.33 eV detected in the phase measurement. Two broad peaks appeared in the range of 2.07-2.35 eV of 2ħω energy for all the samples. These peaks originate from ITO bulk as implied by El-Basaty et al [11]. Since bare ITO gives a small signal at the SHG photon energy of 2.33 eV, the contribution of ITO/organic interface should be relatively large at the same photon energy in Figs. 3(b) and (c) and in the present phase measurement.

Directly using the result in Fig. 2, the phase of SHG from the interface of ITO/organic with respect to the phase observed from ITO, ϕ_{ITO} is determined as

$$\phi_{ITO/organic} - \phi_{ITO} = \frac{2\pi}{\lambda_{2\omega}}\left[\left(n_{2\omega}^{organic} - n_{\omega}^{organic}\right)d\right] + \phi_{ITO/organic,0} \qquad (6)$$

when $\phi_{ITO,0} = 0$. The phase of $\phi_{ITO/organic} - \phi_{ITO}$ is determined to be 59.5 ± 2.82° for ITO/CuPc and 102.94 ± 9.34° for ITO/pentacene. Equation (6) has a phase shift term $\frac{2\pi}{\lambda_{2\omega}}\left[\left(n_{2\omega}^{organic} - n_{\omega}^{organic}\right)d\right]$ emerging from the dielectric dispersion of the organic layer. The value of $n_{2\omega}^{organic} - n_{\omega}^{organic}$ for CuPc thin film is -0.57 and that for pentacene thin film is -0.14 [29, 35]. From here, we calculate the $\frac{2\pi}{\lambda_{2\omega}}\left[\left(n_{2\omega}^{organic} - n_{\omega}^{organic}\right)d\right]$ as -38.6°and -9.5° for CuPc and pentacene, respectively. The value of the $\phi_{ITO/organic,0}$ equals to 98° for ITO/CuPc and that for ITO/pentacene is 112°. The phase shift $\phi_{ITO/organic,0}$ is the phase of $E_{ITO}^{(2\omega)} + E_{interface}^{(2\omega)}$ at ITO/organic interface with respect to the $\phi_{ITO,0}$ = 0°.

3.2 Homodyne Measurement and Fresnel Factor

The result of homodyne measurement is presented as empty squares in Fig. 4. Horizontal axis is the ionization energy of the organic molecules and the work function of ITO. The data was obtained in the same setup as the experiment in Section 3.1, with the α-SiO_2 (0001) reference (PSU) removed. The polarization of the SHG was p-in/p-out. This polarization combination was chosen because the intensities were similar to the 45°-in/p-out SHG intensities. The decrease of SHG detected from ITO/organic compared to that from bulk ITO is expressed in percentage of $\frac{I_{SHG}(ITO)-I_{SHG}(ITO/organic)}{I_{SHG}(ITO)}$.

The Fresnel factor correction was done based on the formalism by Tong et al [36]. Linear transmission and reflectance of p-polarization was used for the analysis of SHG intensity as well as the phase. For ITO/CuPc, there was 4.3% decrease of the observed SHG as seen in Fig. 4 while the decrease of SHG of ITO/CuPc by the Fresnel factor was estimated to be as large as ~ 20 %. So, it is not clear for ITO/CuPc whether the interface SHG has any effect on the total SHG or not, only from this homodyne data. On the other hand, for ITO/pentacene 53.52 % decrease of SHG was observed in Fig. 4, while the decrease of SHG by the Fresnel factor was estimated as 12 % only. Thus, the interface SHG clearly decreased the total SHG in the ITO/pentacene system.

3.3 SHG Phase $\phi_{interface}$ from the Interfaces of ITO/CuPc and ITO/pentacene only

Filled circles in Fig. 4 show the SHG's phase, $\phi_{interface}$ from the ITO/organic interfaces only. This is the phase of $E_{interface}^{(2\omega)}$ obtained after contribution of the bulk ITO is subtracted in the complex plane by using the relation of $E_{sample}^{(2\omega)} = E_{ITO}^{(2\omega)} + E_{interface}^{(2\omega)}$ as shown in Fig. 5 [32]. The complex values of the SHG electric field are drawn as two-dimensional vectors in Fig. 5. The magnitudes of $E_{ITO}^{(2\omega)}$ and $E_{ITO}^{(2\omega)} + E_{interface}^{(2\omega)}$ were obtained from the measured intensity and were normalized by $E_{ITO}^{(2\omega)}$. Finally, we extracted the phase, $\phi_{interface}$ from the interface of ITO/organic only, as shown in the complex plane. The absolute phase from the interface of ITO/CuPc only is approximately 140°, while the interface of ITO/pentacene only has the absolute phase of 160° with respect to the phase of the ITO bulk.

4. Discussion

We suggest three candidate origins of the phase shift from the interface. The first candidate origin is the phase of $\chi^{(2)}$ originating from the static dipole. According to Lalama and Garito [17], the nonlinear susceptibility $\chi^{(2)}$ has generally the same sign as the static dipole. This origin has been implied in the study of MoO_3/α-NPD by El-Basaty and his co-workers and it may also apply to our system [11]. In addition to the phase difference $\pi=180^{o}$ we think of the following two candidate origins.

The second candidate origin is the SHG phase arising from the complex property of the resonant non-linear susceptibility, $\chi_R^{(2)}$ of the interface molecules effective at the measured photon energy. If this origin is operative, the phase shift of ITO/organic will naturally be away from π rad. As pointed out by Suzuki et al and Aktsipetrov et al, the behavior of the phase differences by nonlinear susceptibility $\chi_R^{(2)}$ can only be approached when the phase differences as a function of the photon energy is known [18, 19]. Because our current phase data is obtained at only one photon energy, we cannot get a complete picture of the $\chi_R^{(2)}$ of the interface dipoles. Here, we should note that 2ħω = 2.33 eV lies at the resonance tail of the absorption spectra of CuPc and pentacene molecules. The molecules are not totally off resonance at the SHG photon energy. Thus, the second candidate of phase shift is possible in our measurement.

The third candidate origin of the phase shift is the spatial fluctuation of the interface dipole between the organic molecules and ITO [20]. CuPc and pentacene molecules are capable of becoming cations by giving charge to ITO, and dipoles are formed at the interface [1]. Here can be a spatial fluctuation of charge transfer and dipole density. Generally, fluctuation in optical properties of molecules will create inhomogeneous broadening in the spectrum of the medium and thus imaginary part in the optical response function [20, 37]. It should be related to the fluctuation-dissipation theorem saying that random effects give rise to frictional force [37]. In our case, the fluctuating dipole moments at the interface can lead to the imaginary part of the non-linear susceptibility, *Im* $\chi^{(2)}$ and it then leads to the phase shift.

In this study, the phases of the SHG waves at the ITO/organic interfaces were measured for the organic materials of CuPc and pentacene. The phase shift, $\phi_{ITO/organic,0}$ was calculated to be 98° for ITO/CuPc and 112° for ITO/pentacene. By using complex plane calculation mentioned in Sect. 3.3, the $\phi_{interface}$ has been estimated to be approximately 140° for ITO/CuPc and 160° in ITO/pentacene. These phases from the interface of ITO/organic can be associated with static dipole. Deviation of the phase shifts away from 180° suggests that there is an effect of molecular resonance or spatial fluctuation of the static dipole at the interface.

In previous SHG observation of El Basaty et al of ITO/MoO_3/α-NPD, they observed a negative interference between the ITO substrate and the MoO_3/α-NPD layers in their homodyne measurement [11]. They did not measure the phase of the SHG, but assumed a phase difference of π (180°) between the metal-oxide/organic and bulk ITO. Considering the results in the present work, their assumption was not so bad but might have had some errors.

In a past literature, the SHG phase from the water/air interface relative to quartz was reported to be 115° [23]. The photon energy used in the experiment was non-resonant to the electronic states of the interface materials. However, they did not mention the physical origin of this absolute phase shift and it is a difficult problem.

Intermolecular interaction of charge transfer is expected at the interfaces of the ITO/CuPc and ITO/pentacene due to the lower ionization energy than the work function of ITO [1, 6, 38]. The phase from the dipoles related to the charge transfer has been detected as $\phi_{interface}$ in our SHG phase measurement. Using this new knowledge, we believe it will be possible to check the electronic attributes of the buried interface by more detailed measurement of the SHG phase in the future.

5. Conclusion

By translating α-SiO_2 (0001) as a phase shifting unit along the output line of our optical SHG measurement, we observed the phase shift, $\phi_{ITO/organic,0}$ of 98° and 112° in the SHG response from the interfaces of ITO/CuPc and ITO/pentacene thin film, respectively. Phase shift introduced by dielectric dispersion of the organic thin film was taken into account in analyzing the relative phase difference of the sample ITO/organic. Finally, the analysis of the SHG amplitude in the complex plane shows that the SHG phase from the interface of ITO/CuPc and ITO/pentacene are 140° and 160°, respectively, as measured from that of the bulk ITO. We suggest the static dipoles, the electronic resonance from the interface organic molecules and the spatial fluctuation of the dipole density as feasible candidates of phase shift in our samples.

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Figure Captions

Figure 1 Optical scheme for SHG phase measurement near the sample. In the incident beam path, F1 is a 2ω-cut filter, L1 is a lens of 1200 mm focal length, and P1 is a polarizer with 45° light polarization. In the output beam path, F2 is an ω-cut filter, L2 is a lens of 200 mm focal length, and P2 is a polarizer with p-polarization.

Figure 2 (a) SHG interference pattern of Indium Tin Oxide (ITO). The phase of the pattern of this sample is used as a reference for other samples. (b-c) SHG interference pattern of ITO/organic; CuPc (b) and pentacene (c).

Figure 3 SHG intensity of ITO, ITO/CuPc and ITO/pentacene as a function of the SHG photon energy.

Figure 4 SHG intensity (empty squares) in homodyne SHG measurement and the phase from the interface of ITO/organic only, $\phi_{interface}$ (filled circles) as a function of the ionization energy of the organic films. I_p = 5.02 eV is the work function of ITO.

Figure 5 Vector components of each SHG electric field in the relation $E_{sample}^{(2\omega)} = E_{ITO}^{(2\omega)} + E_{interface}^{(2\omega)}$ in the frame of complex plane. The dashed lines are the magnitude of $E_{interface}^{(2\omega)}$ and the phase, $\phi_{interface}$ from the interface of ITO/organic only.

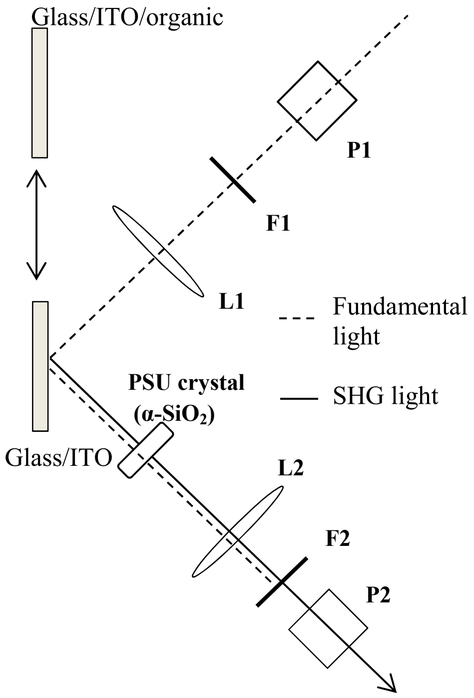
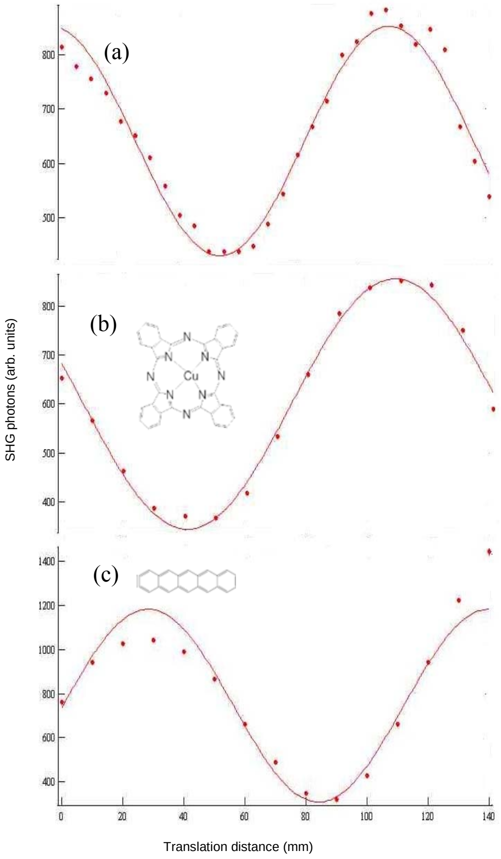


Fig. 1 S. Z. N. Demon et al.



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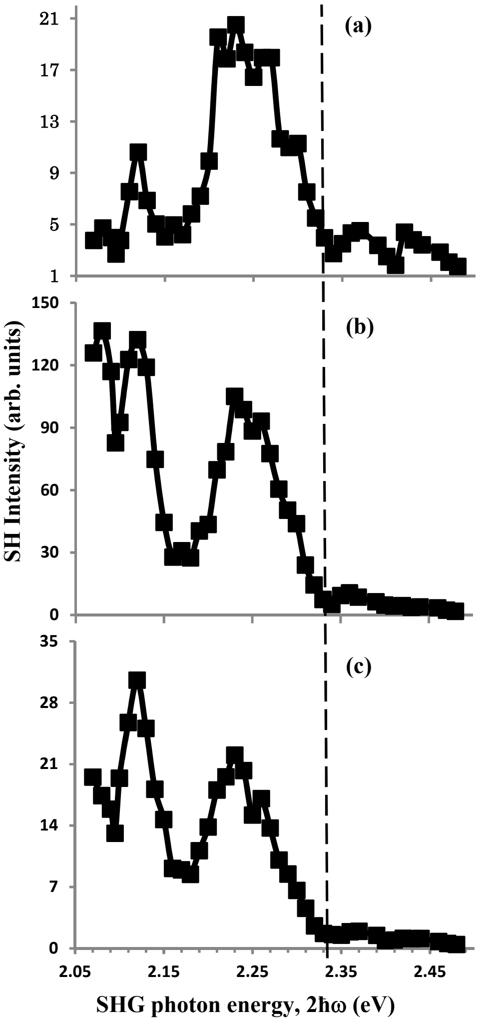

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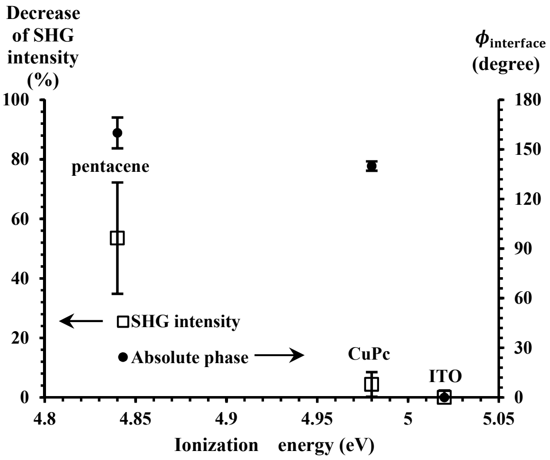

Fig. 4 S. Z. N. Demon et al.

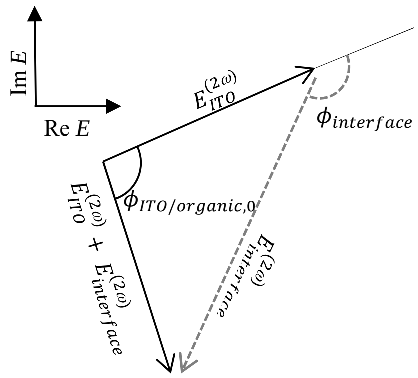

Fig. 5 S. Z. N. Demon et al.