Optical absorption spectrum of pentacene cation radicals measured by charge-modulation spectroscopy

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Abstract

Charge-modulation spectroscopy was applied to vacuum-sublimed films of pentacene in the metal-insulator-semiconductor configuration with Parylene-C or cross-linked polymer as insulator. The spectrum exhibited several peaks in the wavelength range of 300-800 nm. The signal in the visible was ascribed to the field-modulation effect of a neutral pentacene film, while the three broad peaks in the UV exhibited field and frequency dependences different from those in the visible and were ascribed to the optical absorption due to a monocation radical of pentacene. This assignment was supported by the calculation reported earlier on the basis of the time-dependent density functional theory.

Keywords: Pentacene; Cation radical; Charge-modulation spectroscopy; Solid film

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1. Introduction

Electroabsorption spectroscopy with electric field as a periodical perturbation has been used to study charge-transfer excitations of organic molecules in the solid state [1-6]. The observed spectra give the first- or second-derivative of absorption spectra of neutral molecules, reflecting the nature of excited states of molecules. Charge-modulation spectroscopy (CMS) developed first in Cavendish laboratory [7-11] similarly uses a periodical modulation of electric field which was applied to the metal-insulator-semiconductor (MIS) diode. In the CMS, the applied field induces charged species near the insulator-semiconductor interface and absorption spectra of charge carriers in solid states can be measured with a high sensitivity by using the lock-in technique. Up to the present time, the CMS technique has been employed to characterize charged species almost exclusively in polymers or oligomers such as polyacetylene, poly(3-hexylthiophene), and α-sexithiophene [7-13]. Our recent CMS study dealt with *N*,*N*'-diphenyl-*N*,*N*'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) [14], which is a molecule that has been used traditionally as a hole-transporting layer in organic light emitting diodes. Interestingly, the CMS spectra measured with the TPD film in the visible and near-infrared (NIR) showed a sharp peak at 480 nm corresponding well to TPD cation radicals in solution, but no clear peak due to intervalence-charge transfer (IV-CT) was observed in the NIR [15-17]. The lack of the IV-CT band in the CMS spectrum was explained by assuming that conformation of a TPD molecule in the solid film is kept almost unchanged upon one-electron oxidation of TPD molecule to give rise to $TPD^{+\cdot}$. This implies that on the basis of the CMS measurements one can gain information on a conformational change of molecules in solid state upon oxidation. Another possible advantage of the CMS technique over a common spectroscopy can be found in that spectral characterizations of cation radicals are feasible by CMS even though the molecules are insoluble in any solvents so that chemical or electrochemical generation of cation radicals is hardly possible.

In the present CMS study, our attention is focused on pentacene which is well-known to give high-mobility field-effect transistors and has been extensively studied [18-21]. To the best of our knowledge, there are no solvents which can dissolve pentacene stably [22]. Because of this, little is known about physicochemical properties of its cation radical which plays an essential role in the conduction process. Recently, I_2-doping into pentacene film was studied intensively by Brinkmann et al. [23]. They have ascribed electronic transitions at 407 and 990 nm to a cation radical of pentacene. The absorption peaks at 426 and 954 nm have also been reported for pentacene cation radical in Ar matrix at 12 K [24]. In this Letter, CMS measurements of pentacene films are carried out to determine the absorption spectrum of a monocation radical of pentacene at room temperature.

2. Experimental

Pentacene was purchased from Aldrich and used without further purification. Dichloroparacyclophane (diX-C) was donated by Daisan Kasei Co., Ltd. Poly(4-vinylphenol) (PVP) and 1,6-bis(trichlorosilyl)hexane (C_6) used as a cross-linked polymeric insulator (PVP-C_6) were from Aldrich. MIS diodes of the configuration glass/Al/insulator/pentacene/Au were fabricated by first evaporating Al directly onto a precleaned quartz glass plate at 10^{-3} Pa. Parylene-C films were deposited on it from diX-C as described previously [25]. PVP-C_6 films used as another insulator were prepared by spin coating of 1:1 solution of PVP and C_6 in chloroform [26]. Film thicknesses of Parylene-C and PVP-C_6 were controlled to be as thin as 50 nm in order to avoid unwanted signals arising from the combination of an interference and electro-optical Kerr effects [25]. Pentacene films of 40 nm in thickness were sublimed at a rate of 1 Å s^{-1} under the pressure of 10^{-3} Pa or below. Finally, a thin Au film was evaporated over the pentacene film. Nominal thicknesses of Al and Au layers were 10 and 25 nm, respectively. The active area of the pentacene film was 3x3 mm^2. All the measurements were made under ambient atmosphere.

CMS signals were measured in the transmission mode over a wide range of wavelength (300-1400 nm). The CMS spectrometer in the 300-600 nm range consisted of a 500 W Xe lamp, monochromator (Shimadzu SPG-120S: blaze wavelength = 350 nm), photomultiplier tube (Hamamatsu Photonics R928), current-voltage amplifier (NF LI-76) and lock-in amplifier (NF LI-5640). In the CMS measurements of the 600-900 nm range, a light source and a photodetector were replaced with a 150 W tungsten halogen lamp and Si photodiode (Hamamatsu Photonics S1226-5BK), respectively. In the measurements of the 900-1400 nm range, a monochromator and a photodetector used were Shimadzu SPG-120IR (blaze wavelength = 1000 nm) and InGaAs photodiode (Hamamatsu Photonics G8370-03), respectively. The monochromatic light was focused as a 3 mm^2 spot onto the sample normal to the surface. A sinusoidal voltage oscillating between 0 and V_p was applied to the MIS diode by amplifying the internal oscillator output from the lock-in amplifier using a piezo driver (Mess-Tek M-2633). The peak modulation voltage (V_p) applied to the Al electrode was negative so as to build up an accumulation layer in the pentacene film near the insulator/pentacene interface. The sign of the voltage corresponds to the generation of cation radicals. The modulation frequency (f) was the same as the reference frequency of the lock-in amplifier, and in-phase and quadrature components of the lock-in signal were recorded. Wavelength scanning and data acquisition from the lock-in amplifier were automatically made with a personal computer via I/O port and RS232C interface. The intensity of a monochromatic light passing through the MIS diode was measured simultaneously with the lock-in signal and the intensity ratio of the modulated light to the transmitted light was processed to give the CMS signal ($-\Delta T/T$) as a function of wavelength. Here, T denotes transparency. Measurements of a series resistance and capacitance for the MIS diodes were made at different bias voltages at f = 100 Hz using LCR meter (Hioki 3522). All the measurements were made under ambient atmosphere.

3. Results and discussion

Fig. 1 depicts in-phase and quadrature components of the CMS signal for the pentacene MIS diode measured at f = 100 Hz and V_p = -5 V in the wide wavelength range of 300-1400 nm, where the signal is rotated by 24^o so as to minimize the quadrature component over the wavelength range studied. Several peaks are seen in the in-phase CMS signal, whereas the quadrature component is much smaller than the in-phase one and exhibits no characteristic peaks. These spectral features were kept unchanged when the modulation voltage and frequency were varied, although the phase offset was increased with an increased modulation frequency as in the case of TPD [14]. The large delay of the CMS signal is ascribable to a large contact resistance of Au/pentacene film (ca. 100 kΩ) coupled with a series capacitance of ca. 30 nF measured with the MIS diode biased at -5 V.

The CMS signal for the pentacene MIS diode with CPVP-C_6 as insulator is shown in Fig. 2. Irrespective of the sort of insulating layers, the quadrature component is negligibly small and independent of wavelength when the phase is rotated by 9^o. Furthermore, the spectral feature of the in-phase signal has a close agreement with the one observed with Parylene-C. As shown in the inset, the pentacene film has a strong absorption in the UV and visible regions. The absorption of light can induce a field-modulation effect in the corresponding wavelength range and the resulting spectrum is known to be represented by the first and/or second derivative of the absorption spectrum of the neutral film. When the in-phase signal is compared with the first derivative of the absorption spectrum of the pentacene film, close similarities of the peak positions in the 500-700 nm range can be readily found, demonstrating that the peaks with positive and negative signs appearing in this wavelength range are ascribable to the field-modulation effect [1-6]. On the other hand, the CMS signal ($-\Delta T/T$) in the 300-450 nm range is negative, corresponding to absorption of light. It consists of a few broad peaks different in wavelength from the one expected from the field-modulation effect. This suggests that the CMS spectrum in the 300-450 nm range can not be accounted for in terms of the field-modulation effect. Another distinction between the CMS and the derivative spectra is seen in the wavelength range beyond 700 nm: the CMS signal decreases gradually up to, at least, 1400 nm, whereas no absorption is seen in the spectrum of the neutral pentacene film.

Fig. 3 depicts dependences of the CMS signals at 420 and 600 nm on frequency as well as V_p. As shown in Fig. 3(a), the 420-nm signal increases slightly with the decrease in V_p and starts to increase more rapidly at around -1.5 V. This trend is similar to the V_p dependence of the CMS signal for the TPD MIS diodes [14]. In contrast, the V_p dependence of the signal at 600 nm fits a single straight line and is different from the 420 nm-signal, suggesting that the origins of the signals at the two wavelengths differ from each other. The different natures of the two signals can be more clearly noted in the f dependence of the CMS signals shown in Fig. 3(b). The 420-nm signal decreases with the increase of f, whereas the 600-nm signal increases as f increases. On these bases, it is reasonable to assume that the signal in the UV is due to the charge-modulation effect and the signal in the visible originates from the field-modulation effect. It is known that the field-modulation signal is in proportion to the square of V_p [5,6,27], different from the linear dependence in our observations. In our MIS diode configuration, the voltage applied to the pentacene film is compensated in part by the build-up of the accumulation layer near the insulating layer, and thus a uniform electric field throughout the entire molecular film may not be formed. This may explain the observed V_p dependence of the field-modulated signal being different from the one theoretically predicted and experimentally observed.

To gain a precise spectral feature of pentacene cation radicals, measurement conditions to give better-resolved CMS spectra were examined by, for example, decreasing the scanning rate of wavelength along with the increase of the time constant of the lock-in amplifier. Deuterium lamp which enables a stable illumination of UV light was also attempted, although the S/N ratio of the CMS signal was not improved because of low light intensities compared with the optical system comprising the Xe lamp. Fig. 4 shows the CMS signal (in-phase component) of the pentacene MIS diode measured in the 300-460 nm range under the optimal conditions. Unfortunately, we were forced to discuss the CMS signal only in this wavelength range, because the CMS signal in the visible were likely to be complicated by the field-modulation effect. The slow decaying part of the CMS signal in the 700-1400 nm, where no considerable influence of the field-modulation effect can be expected, might include a component due to the charge-modulation effect. However, we will not discuss the signal in the NIR further, because we have found for the TPD MIS diode that the CMS signal intensities in this region are not zero because of unknown reasons [14]. The measured CMS spectrum consists of three broad absorption peaks centered at 335, 370, and 415 nm. Up to the present time, a few experimental studies have addressed optical features of monocation radicals of pentacene. Szczepanski et al. generated pentacene cations by electron bombardment of a vapor phase mixture of pentacene, Ar, and CCl_4, and assigned the absorption bands at 426 and 954.1 nm in Ar matrix at 12 K to the pentacene cations [24] on the basis of comparisons with the photoelectron spectrum of pentacene [28]. Halasinski et al. with a photolytic technique have observed 420.5-nm band in Ne and 425.1-nm band in Ar at 4.2 K [29], together with several NIR absorption peaks in the Ne, Ar, and Kr matrices agreeing well with those of the study by Szczepanski et al. [24]. More recently, Brinkmann et al. oxidized the evaporated film of pentacene by I_2 at room temperature and assigned the 407-nm and 993-nm bands to the cation radical of pentacene, although the spectrum in the UV and visible was strongly disturbed by the strong absorption background due to the enhanced reflectivity and scattering of the film by I_2-doping [23]. The additional band at 370 nm was ascribed to polyiodides such as I_3^- and I_5^- which show strong absorptions in the wavelength range between 360 and 430 nm [30]. All the previous experimental studies report a single absorption peak in this wavelength region for pentacene cation radicals, in contrast to three absorption peaks in this study. Based on the time-dependent density functional theory, Hirata et al. have reported excitation energies (E_x) and oscillator strengths (*F*) for cation radicals of polycyclic aromatic hydrocarbons including pentacene [31]. For pentacene cation radical, E_x values are 2.57 (482), 2.88 (431), and 3.08 eV (403 nm) with F = 0.021, 0.007 and 0.066, respectively. The three broken curves in Fig. 4 represent Gaussian distribution functions calculated with the data of E_x and *F*, where the areas of the curves correspond to the respective *F* values with their spectral shapes in energy scale being kept the same. The theoretical absorption spectrum of pentacene cation radial as the sum of the three absorption components resembles well the CMS spectrum shown in Fig. 4, although the CMS spectrum is shifted by ca. 0.6 eV to a shorter wavelength side. The close coincidence between the shapes of the CMS and calculated spectra demonstrates strongly that the CMS spectrum in the 300-460 nm range gives the absorption spectrum of a monocation radical of pentacene.

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References

[1] S.C. Abbi, D.M. Hanson, J. Chem. Phys. 60 (1974) 319.

[2] N.A. Kirichenko, L.M. Blinov, Zh. Prikl. Spektrock. 28 (1978) 1057.

[3] L. Sebastian, G. Weiser, H. Bässler, Chem. Phys. 61 (1981) 125.

[4] A. Chowdhury, S.A. Locknar, L.L. Premvarhran, L. Peteanu, J. Phys. Chem. A. 103 (1999) 9614.

[5] T. Nakabayashi, M. Wahadoszamen, N. Ohta, J. Amer. Chem. Soc. 127 (2005) 7041.

[6] W. Stampor, W. Mróz, Chem. Phys. 331 (2007) 261.

[7] J.H. Burroughs, C.A. Jones, R.H. Friend, Nature 335 (1988) 137.

[8] K.E. Ziemelis, A.T. Hussain, D.D.C. Bradley, R.H. Friend, Phys. Rev. Lett. 66 (1991) 2231.

[9] M.G. Harrison, K.E. Ziemelis, R.H. Friend, P.L. Burn, A.B. Holmes, Synth. Met. 55-57 (1993) 218.

[10] H. Sirringhaus, P.J. Brown, R.H. Friend, M.M. Nielsen, K. Bechgaard, B.M.W. Langeveld-Voss, A.J.H. Spiering, R.A.J. Janssen, E.W. Meijer, P. Herwig, D.M. de Leeuw, Nature 401 (1999) 685.

[11] D. Beljonne, J. Cornil, H. Sirringhaus, P.J. Brown, M. Shkunov, R.H. Friend, J-L. Brédas, Adv. Funct. Mater. 11 (2001) 229.

[12] F. Charra, D. Fichou, P.-A. Chollet, D. Paquet, Synth. Met. 81 (1996) 173.

[13] M.G. Harrison, D. Fichou, F. Garnier, A. Yassar, Opt. Mater. 9 (1998) 53.

[14] Y. Harima, Y. Ishiguro, Y. Fujikawa, T. Hashiguchi, K. Komaguchhi, Y. Ooyama, I. Imae, J. Ohshita, Chem. Phys. Lett., 485 (2010) 100.

[15] P.J. Low, M.A.J. Paterson, H. Puschmann, A.E. Goeta, J.A.K. Howard, C. Lambert, J.C. Cherryman, D.R. Tackley, S. Leeming, B. Brown, Chem. Eur. J. 10 (2004) 83.

[16] B.S. Brunschwig, C. Creutz, N. Sutin, Chem. Soc. Rev., 31 (2002) 168.

[17] C. Lambert, G. Nöll, J. Am. Chem. Soc., 121 (1999) 8434.

[18] N. Koch, A. Kahn, J. Ghijssen, J.-J. Pireaux, J. Schwartz, R.L. Johnson, A. Elschner, Appl. Phys. Lett., 82 (2003) 70.

[19] L. Wang, D. Fine, T. Jung, D. Basu, H. von Seggern, A. Dodabalapur, Appl. Phys. Lett., 85 (2004) 1772.

[20] M. Halik, H. Klauk, U. Zschieschang, G. Schmid, C. Dehm, M. Schütz, S. Maisch, F. Effenberger, M. Brunnbauer, F. Stellacci, Nature, 431 (2004) 963.

[21] T.G. Bäcklund, R. Österbacka, H. Stubb, J. Bobacka, A. Ivaska, J. Appl. Phys., 98 (2005) 074504.

[22] K.S. Kang, Y. Chen, H.K. Lim, K.Y. Cho, K.J. Han, J. Kim, Thin Solid Films, 517 (2009) 6096.

[23] M. Brinkmann, V.S. Videva, A. Bieber, J.J. André, P. Turek, L. Zuppiroli, P. Bugnon, M. Schaer, F. Nuesch, R. H-Baker, J. Phys. Chem. A, 108 (2004) 8170.

[24] J. Szczepanski, C. Wehlburg, M. Vala, Chem. Phys. Lett., 232 (1995) 221.

[25] Y. Harima, T. Hashiguchi, Y. Fujikawa, K. Komaguchi, Y. Ooyama, I. Imae, Chem. Phys. Lett. 457 (2008) 115.

[26] M-H. Yoon, H.Yan, A. Facchetti, T.J. Marks, J. Am. Chem. Soc., 127 (2005) 10388.

[27] P. Petelenz, A. Stradomska, Phys. Rev. B, 71 (2005) 235205.

[28] W. Schmidt, J. Chem. Phys., 66 (1977) 828.

[29] T.M. Halasinski, D.M. Hudgins, F. Salama, L.J. Allamandola, T. Bally, J. Phys. Chem. A, 104 (2000) 7484.

[30] P.P.F. de Violet, R. Bonneau, J. Joussot-Dubien, J. Chim. Phys., 72 (1975) 855.

[31] S. Hirata, M. Head-Gordon, J. Szczepanski, M. Vala, J. Phys. Chem. A, 107 (2003) 4940.

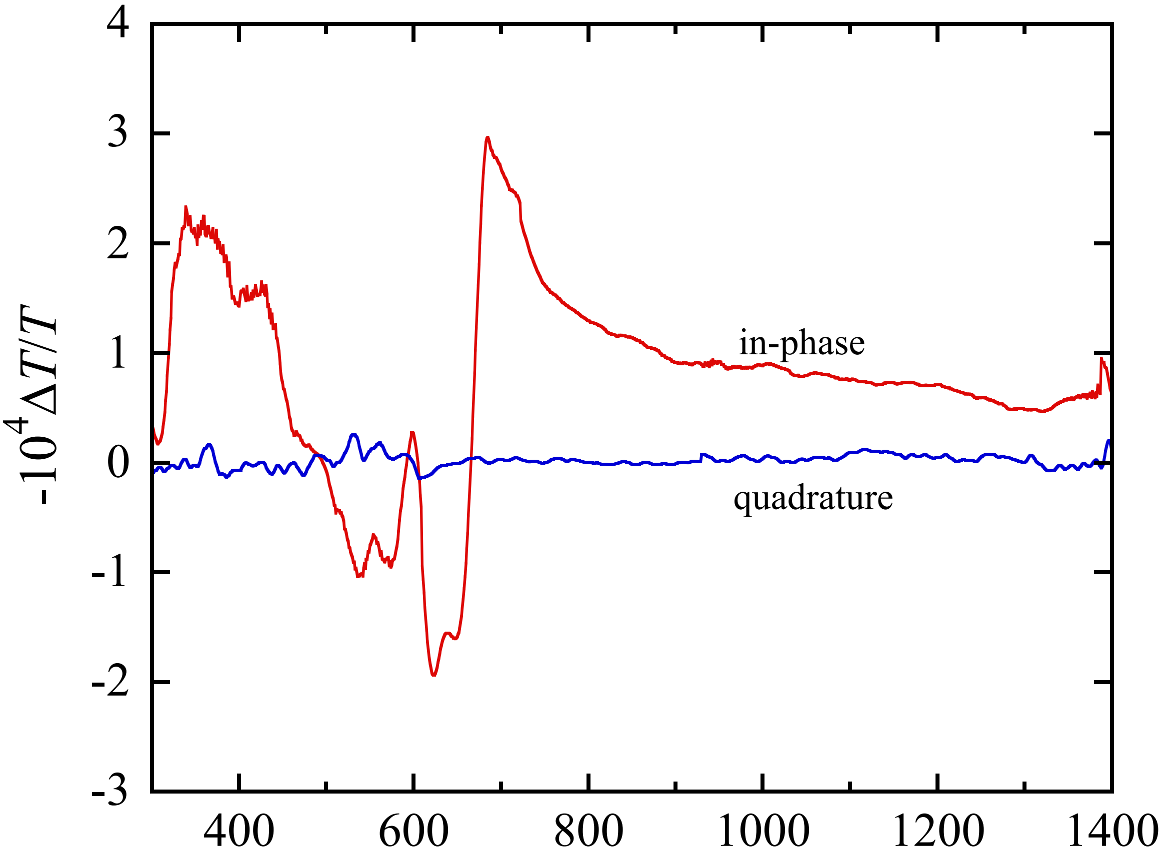
Figure captions

Fig. 1. CMS spectra of Al (10 nm)/Parylene-C (50 nm)/pentacene (40 nm)/Au (25 nm) MIS diode at f = 100 Hz and V_P = -5 V, where in-phase and quadrature signals are rotated by 24° to minimize the quadrature component.

Fig. 2. CMS spectra of Al (10 nm)/CPVP-C_6 (50 nm)/pentacene (40 nm)/Au (25 nm) MIS diode at f = 100 Hz and V_P = -6 V, together with the first derivative of absorption spectrum of pentacene film (40 nm) deposited on quartz substrate. The inset shows the absorption spectrum of pentacene film.

Fig. 3. Dependences of CMS signal intensities at 420 and 600 nm (a) on V_p at f = 200 Hz and (b) on f at V_p = -6 V for Al (10 nm)/CPVP-C_6 (50 nm)/pentacene (40 nm)/Au (25 nm) MIS diode.

Fig. 4. CMS spectrum of Al (10 nm)/Parylene-C (50 nm)/pentacene (40 nm)/Au (25 nm) MIS diode at f = 100 Hz and V_P = -6 V. Smooth solid curve denotes absorption spectrum of pentacene cation radical obtained as the sum of three absorption components (broken curves) calculated with the literature data [31].



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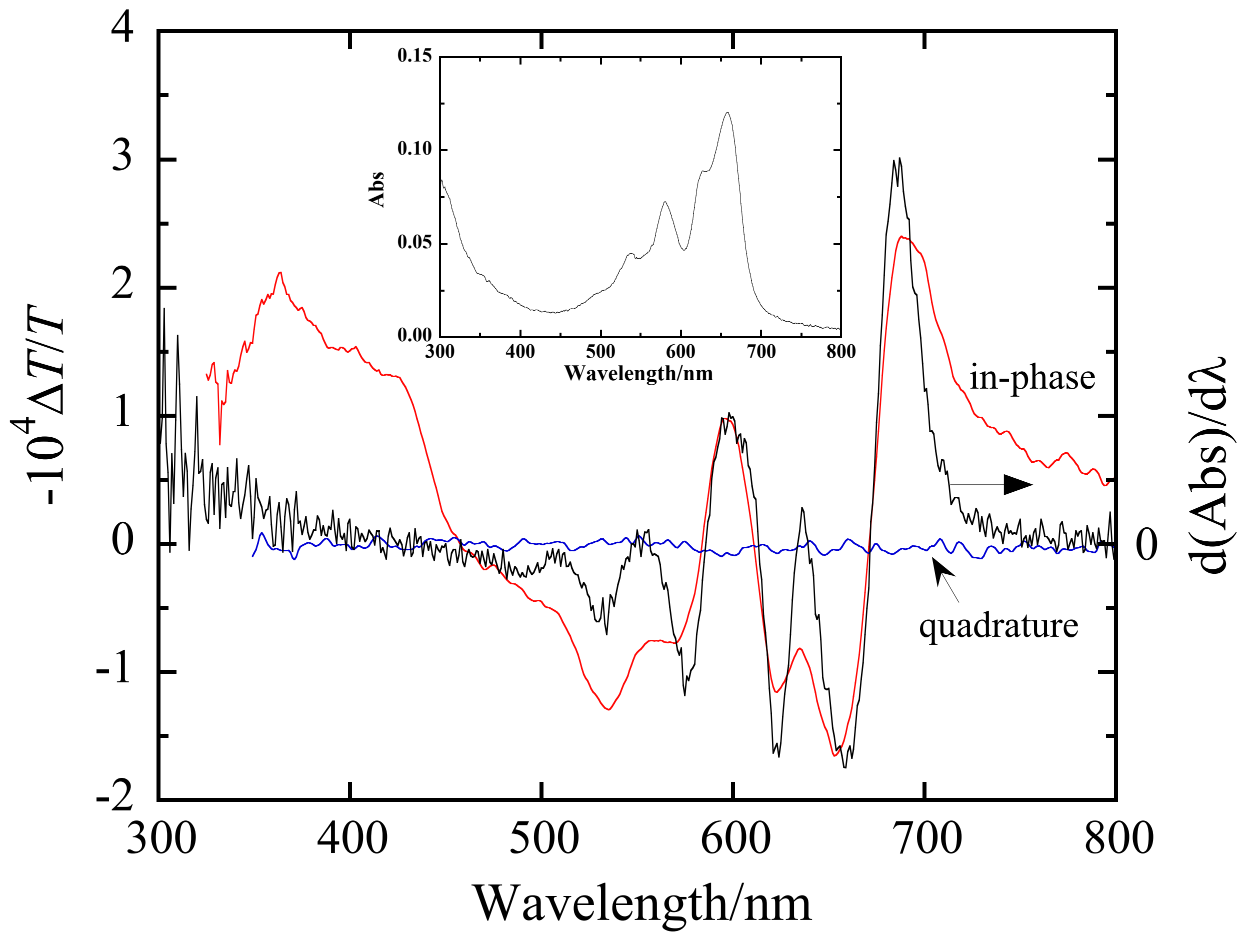

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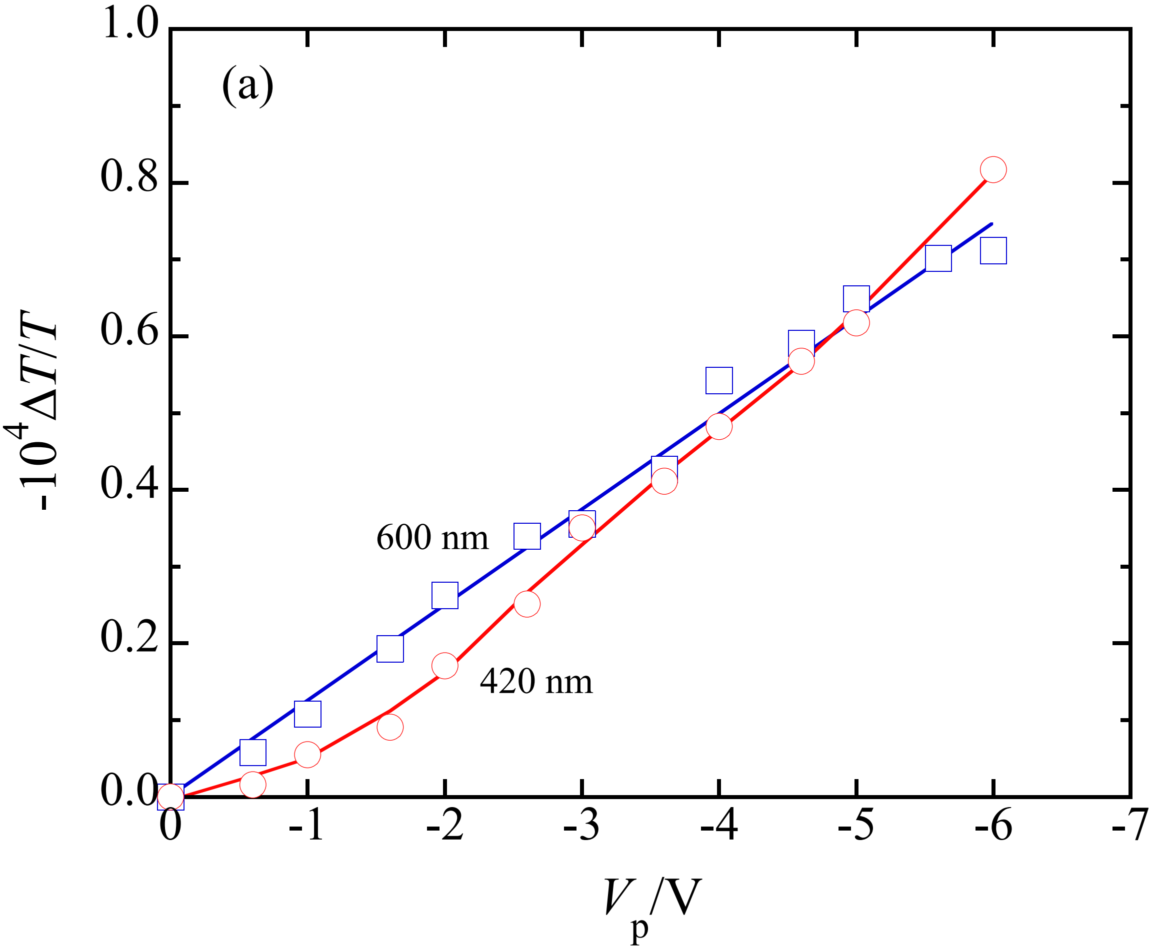

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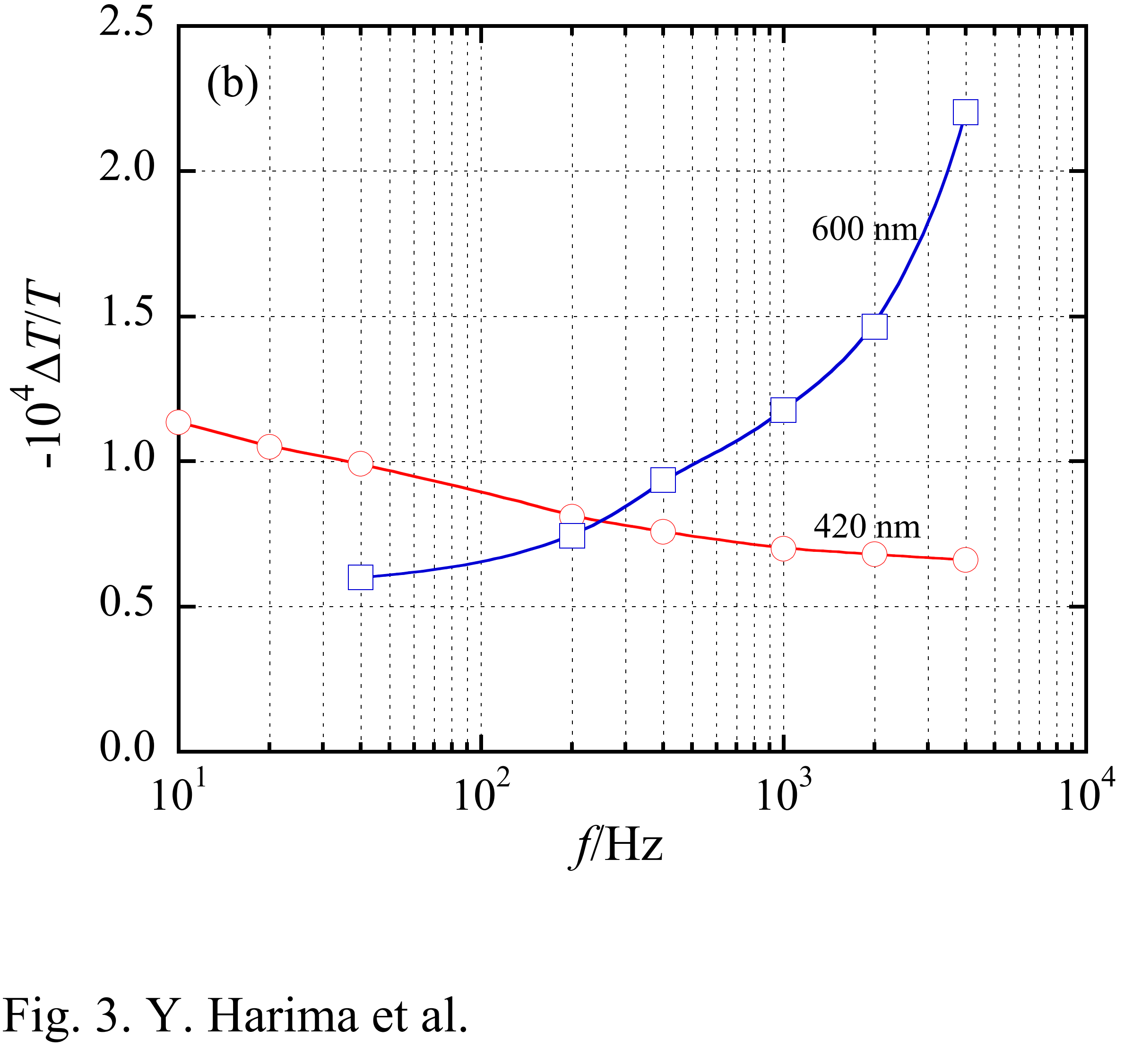

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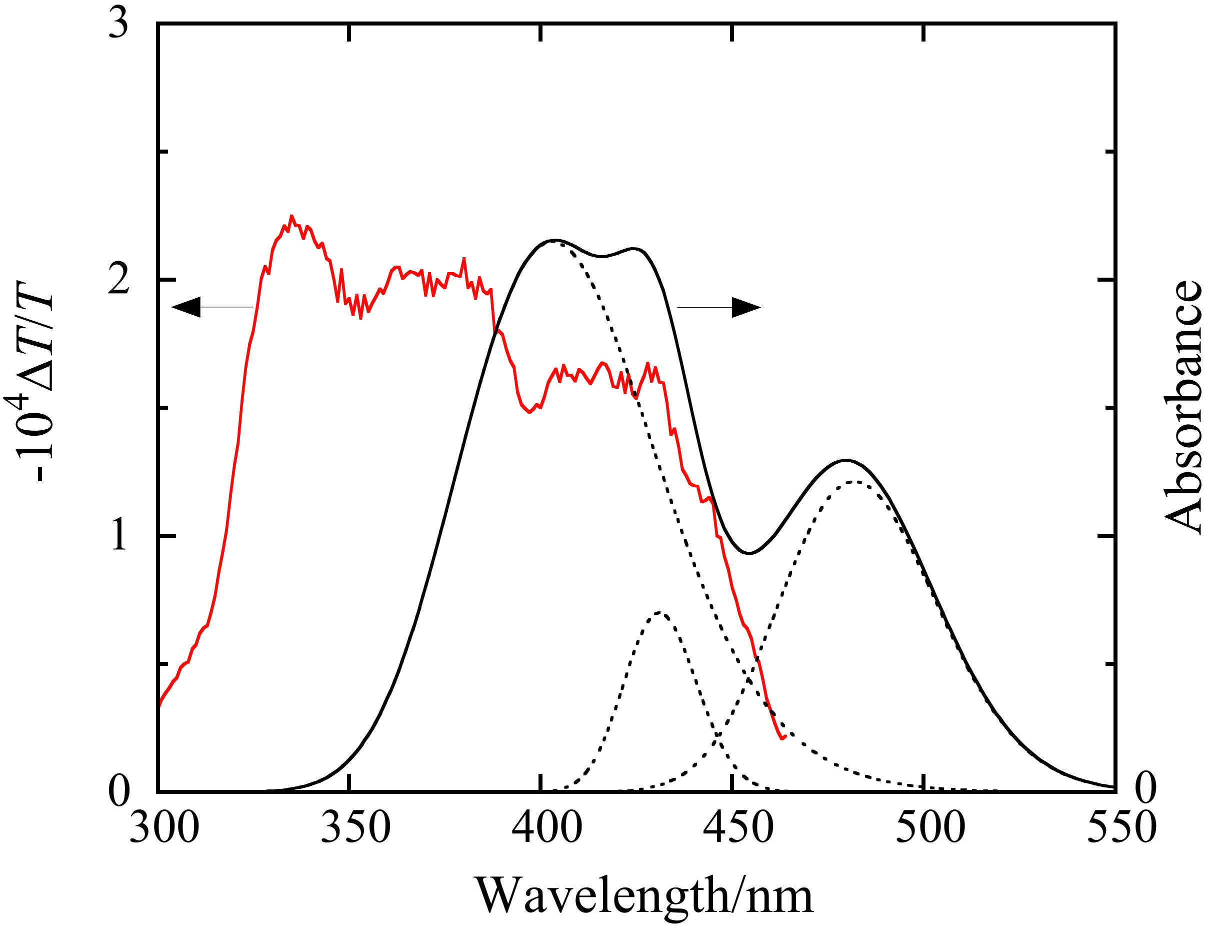

Fig. 4. Y. Harima et al.