

Simultaneous multi-photon ionization of aromatic molecules
in polymer solids with ultrashort pulsed lasers

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Abstract

Radical cations of perylene, terthiophene, *N,N,N',N'*-tetramethylbenzidine, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, and *N*-ethylcarbazole were formed in poly(methyl methacrylate) solids by the direct excitation of each absorption band with a 355-nm picosecond (ps) laser and a 400-nm femtosecond (fs) laser and also by the indirect excitation with a 800-nm fs laser. The photoionization yields of perylene with ps and fs lasers were independent of the concentration of tetracyanobenzene, indicating that the relaxed singlet excited state of perylene is not involved in the photoionization. These results show that radical cations are formed through simultaneous multi-photon ionization enhanced by resonance with the lowest singlet excited state.

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1. Introduction

Since the advent of ultrashort pulsed lasers, ultrafast spectroscopic and non-linear optical studies have made rapid progress.[1,2] Furthermore, the development of high-intensity pulsed lasers has opened the door to new research fields on photoionization such as resonance-enhanced multi-photon ionization ($< 10^{13} \text{ W cm}^{-2}$), non-resonant multi-photon ionization ($\sim 10^{13} \text{ W cm}^{-2}$), optical field ionization ($\sim 10^{14} \text{ W cm}^{-2}$, which corresponds to the electric field strength of several $\text{V \AA}^{-1}$ and will therefore disturb the molecular potential significantly) and Coulomb explosions ($> 10^{16} \text{ W cm}^{-2}$) [3]. In general, multi-photon ionization of aromatic molecules with high intensity lasers has been studied by time-of-flight mass spectroscopy [2,3] in the gas phase and by the photocurrent method [4,5] in the liquid phase. The number of photons involved in the ionization process can be evaluated from the slope of the log-log plots of the ion yield against the laser intensity. Recently, high-order multi-photon fluorescence of organic molecules in solutions has been reported by using near-IR fs laser pulses.[6]

In contrast, there are only few reports on the multi-photon ionization of isolated aromatic molecules in solids, because the parent cation formed in solids cannot be detected by either time-of-flight mass spectroscopy or the photocurrent method. In our two-photon ionization of aromatic molecules doped in polymer solids [7,8], however, stable radical cations of the dopant molecules were easily detected as coloration formed in such solids, because photoejected electrons from the dopant were captured by electron-accepting groups of the polymer matrix. As a result, the coloration could be observed even after storage of two years at room temperature, indicating potential applications to optical recording. Tsuchida et al. reported that electron acceptors added as an electron scavenger could capture the electrons ejected from the dopants and quench the singlet excited state that is an

intermediate state for the two-photon ionization in poly(methyl methacrylate) (PMMA) solids.[8] In other words, the electron scavenging method provides information not only on the ionization yield but also on the intermediate state involved in the ionization process.

In the present Letter, we have studied photoionization of several aromatic molecules in PMMA solids with ultrashort pulsed lasers. Consequently, we found multi-photon ionization of aromatic molecules, in which more than two photons are involved. On the basis of electron scavenging and time-resolved spectroscopic experiments, we discuss the mechanism of multi-photon ionization.

2. Experimental

2.1. Materials

Five kinds of aromatic molecules were employed as a dopant in polymer solids: perylene (Pe, Aldrich), 2,2':5',2''-terthiophene (3T, Aldrich), *N*-ethylcarbazole (EtCz, Tokyo Chemical Industry Co., Ltd.), *N,N,N',N'*-tetramethylbenzidine (TMB, Wako Pure Chem. Ind., Ltd.), *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD, Aldrich). Perylene was purified by silica-gel flash column chromatography using dichloromethane for elution. *N*-Ethylcarbazole, TMB, and TMPD were purified by recrystallization several times. 2,2':5',2''-Terthiophene was used without further purification. Poly(methyl methacrylate) used for block samples was prepared by bulk polymerization of methyl methacrylate. Methyl methacrylate monomer (MMA, Nacalai Tesque) was washed with a 5% NaOH aqueous solution twice and with a 20% NaCl aqueous solution four times, dried with Na₂SO₄ for one day, and then distilled under reduced pressure. For spin-coating films, PMMA (Scientific Polym. Prod., Inc., $M_w = 395000$, $T_g = 378$ K) was purified by reprecipitation from a benzene solution into methanol three times.

1,2,4,5-Tetracyanobenzene (TCNB, Tokyo Chemical Industry Co., Ltd.) was used as an electron acceptor after purification of recrystallization from ethanol.

2.2. Sample preparation

For the photoionization experiment, a block sample of PMMA doped with an aromatic molecule was prepared by bulk polymerization of MMA in a Pyrex cell ($1 \times 1 \times 5$ cm³). Details have been described in Ref. [8]. The absorbance of the aromatic molecule in the PMMA block was adjusted to be around unity at an excitation wavelength of 355 or 400 nm. For the fluorescence quenching and transient absorption experiments, a PMMA block and a PMMA film were prepared as follows. The PMMA block was prepared by bulk polymerization of MMA with Pe and TCNB. The concentration of TCNB in the PMMA block was varied from 0 to 40 mM while that of Pe was kept constant at 0.2 mM. The PMMA film was coated on a quartz plate with a spin coater (Mikasa, Spinner 1H-D2) from a benzene solution (Wako, spectroscopic grade) containing 5 wt% PMMA with Pe and TCNB. The concentrations of the dopant aromatic molecules were adjusted to be 1 mM for Pe and 0 – 40 mM for TCNB in the final polymer film. The film thus obtained was dried by evaporation at room temperature. The thickness of the PMMA film was ~ 1 μ m.

2.3. Measurements

Photoionization of an aromatic molecule in a polymer solid was performed with the following pulsed laser systems: One was a ps Nd:YAG laser (EKSPLA, PL-2400B, ~ 20 ps, 355 nm, ~ 10 mJ cm⁻²; 532 nm, ~ 10 mJ cm⁻²; 1064 nm, ~ 5 mJ cm⁻²). The other was a fs Ti:sapphire laser (Spectra-Physics, Hurricane, ~ 100 fs, 400 nm, ~ 0.5 mJ cm⁻²; 800 nm, ~ 8 mJ cm⁻²). Absorption and fluorescence spectra were measured with a spectrophotometer (Hitachi,

U-3500) and a fluorescence spectrophotometer (Hitachi, F-4500), respectively, at room temperature. Fluorescence decay was measured by the time-correlated single-photon-counting method. Details have been described in Ref. [9]. Femtosecond transient absorption spectra and decay were measured as described in Ref. [10].

3. Results and discussion

3.1. Photoionization of aromatic molecules in PMMA solid

3.1.1. Picosecond laser. Picosecond laser excitation at 355 nm of a PMMA block doped with an aromatic molecule produced the corresponding radical cation. Figure 1 shows absorption spectra of PMMA blocks doped with various aromatic molecules after the photoirradiation at room temperature. All the absorption bands, which were assigned to the radical cations of the dopant aromatic molecules, were independent of the excitation source employed in this study.

The ionization potential of aromatic molecules in the solid state IP_s is calculated by Eq. (1) [11]

$$IP_s = IP_g + P_+ + V_0 \quad (1)$$

where IP_g is the ionization potential of aromatic molecules in the gas phase, P_+ is the polarization energy in the solid state, and V_0 is the bottom energy of the conduction band in the solid matrix. The polarization energy P_+ is evaluated by the Born equation,

$$P_+ = -\frac{e^2}{8\pi\epsilon_0 r_+} \left(1 - \frac{1}{\epsilon_{op}} \right) \quad (2)$$

where e is the elementary charge, ϵ_0 is the vacuum permittivity, ϵ_{op} is the optical dielectric constant of the solid matrix, and r_+ is the radius of the radical cation evaluated from the van der Waals volume of the aromatic molecule [12]. As listed in Table 1, the IP_g values of the aromatic molecules employed range from 6.5 to 7.7 eV, while the P_+ values are ~ -1.0 eV.

The correct value of V_0 of the PMMA solid is yet unknown, but it is probably > 0 eV because it is reported to be positive, ranging from 0.34 to 1.00 eV for various solid solvents [19]. Here the value of V_0 is assumed to be 0 as a lower limit, and thus the IP_s values of the dopant molecules in the PMMA solid is expected to exceed 5.5–6.6 eV. The one-photon energy of 355-nm light is as low as 3.5 eV, which is insufficient to ionize the aromatic molecules listed in Table 1 but can excite them to their lowest excited states. In other words, the ionization of these aromatic molecules can be resonated with the lowest singlet excited state. Therefore, the formation of radical cations in the PMMA solid is ascribed to resonant two-photon ionization, as we have reported previously for a nanosecond (ns) laser system [8].

On the other hand, no radical cations were observed after the photoirradiation at 532 or 1064 nm with the ps laser. The one-photon energies of 532 and 1064 nm (2.3 and 1.2 eV) are insufficient to excite these molecules even to the lowest excited state. Thus, resonant multi-photon absorption is required to ionize the aromatic molecules in the PMMA solid with the ps laser. No radical cations were observed even at high power irradiation of $5 \times 10^{10} \text{ W cm}^{-2}$. Instead, a cracking was formed at the focus point in the PMMA bulk sample at high power irradiation. This suggests that the thermal energy, rapidly generated at the focal point during the laser excitation, caused thermal bleaching of radical cations.

3.1.2. Femtosecond laser. Femtosecond laser excitation at 400 nm also produced all the radical cations of Pe, 3T, TMB, TMPD, and EtCz in the PMMA solid under an excitation

intensity of $\sim 5 \times 10^9 \text{ W cm}^{-2}$. Figure 2a shows absorption spectra of Pe and EtCz radical cations formed in the PMMA solid by the laser irradiation at room temperature. The first two molecules, Pe and 3T, have absorption at 400 nm, but the rest, TMB, TMPD and EtCz, do not. Thus, the ionization of Pe and 3T is ascribed to the resonant two-photon ionization in which the lowest singlet excited state is involved. On the other hand, the ionization of TMB, TMPD, and EtCz can be ascribed to resonance-enhanced two-photon ionization, because the absorption edges ($\sim 3.4 \text{ eV}$ for TMB, $\sim 3.3 \text{ eV}$ for TMPD, $\sim 3.5 \text{ eV}$ for EtCz) are close to the energy of 400-nm photon (3.1 eV). The two-photon energy of 400-nm light, 6.2 eV , is comparable to or higher than the IP_s values of these aromatic molecules. In other words, the lowest singlet excited state is involved in the photoionization of these aromatic molecules by the fs laser irradiation at 400 nm depending on the optical bandgap.

Furthermore, fs laser excitation at 800 nm also produced radical cations of all the aromatic molecules in the PMMA solid under higher excitation intensities of $\sim 10^{11} \text{ W cm}^{-2}$. Figure 2b shows the absorption spectra of Pe and EtCz radical cations formed in the PMMA solid by the laser irradiation at room temperature. Judging from the photon energy, at least four photons are required for the ionization of the aromatic molecules in PMMA solids because the one-photon energy of 800-nm light is as low as 1.55 eV . The radical cations of Pe and 3T were formed at a slightly lower intensity ($\sim 8 \times 10^{10} \text{ W cm}^{-2}$) than those of TMB, TMPD, and EtCz ($\sim 3.2 \times 10^{11} \text{ W cm}^{-2}$). Both Pe and 3T have absorption at 400 nm, corresponding to the two-photon energy of 800-nm light. Thus, the multi-photon ionization of Pe and 3T can probably be ascribed to resonance-enhanced multi-photon ionization, in which the lowest singlet excited state is produced as an intermediate by the two-photon absorption [5], namely resonance-enhanced (2+2) ionization. On the other hand, the ionization of TMB, TMPD, and EtCz cannot directly resonate with the lowest singlet excited

state, and therefore, requires higher excitation intensity than that of Pe and 3T. Although the laser power of fs laser excited at 800 nm ($8 \times 10^{10} \text{ W cm}^{-2}$) is comparable to that of the ps laser excited at 532 nm ($5 \times 10^{10} \text{ W cm}^{-2}$), as mentioned above, the total energy per pulse of the fs laser ($\sim 10 \text{ mJ cm}^{-2}$) is two orders of magnitude lower than that of the ps laser ($\sim \text{J cm}^{-2}$). Therefore, we conclude that one can lead to multi-photon ionization without thermal damage to the polymer matrix and radical cations with a fs laser even high-power excitation at longer wavelengths where there is no absorption of aromatic molecules, because of the low energy due to the short period irradiation. The photoionization process of these aromatic molecules in PMMA solids is summarized in Table 2.

3.2. Fluorescence quenching and time-resolved measurements

To determine whether the relaxed singlet excited state participates in the photoionization with ps and fs lasers, we have examined the fluorescence quenching of Pe by a TCNB acceptor. Tsuchida et al. [8] reported that the radical cation yield formed by photoirradiation with a ns laser decreased with an increase in the concentration of TCNB acceptor, because the cation formation through a step-wise two-photon ionization competes with electron transfer from the excited state to the acceptor. Here we performed the same quenching experiment for Pe in PMMA films doped with TCNB with ps and fs lasers. Figure 3 shows the yields of Pe radical cation and TCNB radical anion in the PMMA solid with an increase in the concentration of TCNB after the photoexcitation with ps and fs lasers. Note that these radical ions are formed by multi-photon excitation instead of one-photon excitation, as described below. Contrary to the ns laser experiment, the yield of Pe radical cation did not decrease but kept a constant value over the whole concentration range measured. This finding suggests that the relaxed singlet excited state of Pe is not involved in the photoionization process with the ultrashort pulsed lasers.

Figures 4a and 4b show fluorescence spectra and decay of PMMA films doped with Pe and TCNB, respectively. The fluorescence intensity decreased with increasing TCNB concentration. On the contrary, as shown in Figure 4b, the fluorescence decay remained unchanged although the photon counts decreased with the increase in the TCNB concentration. Therefore, the fluorescence quenching is mainly ascribed to the static quenching by one-photon excitation, which is too fast to be detected by our SPC system. We have furthermore measured fs transient absorption spectra to estimate the static quenching rate in PMMA doped with Pe and TCNB. For a PMMA block doped with only Pe, as shown in Figure 5a (broken line), a sharp absorption band was observed at 700 nm [20] immediately after the laser excitation, which are attributed to $S_n \leftarrow S_1$ absorption. For a PMMA block doped with Pe and TCNB, on the other hand, additional absorption bands were observed at 550 and 740 nm, as shown in Figure 5a (solid line). These bands agree well with that of Pe radical cation (dotted line), suggesting that the static quenching of Pe by TCNB results in rapid formation of Pe radical cation within the laser pulse width 100 fs (Scheme 1a). We should note that the Pe radical cation observed by the fs transient absorption spectroscopy is formed by one-photon excitation instead of multi-photon excitation, because the excitation intensity is as low as $\sim 10^7 \text{ W cm}^{-2}$. Figure 5b shows the time evolution of the transient absorption at 550 nm, which represents the formation dynamics of Pe radical cation. Immediately after the laser excitation, 70 % of the Pe radical cation is already formed, and the remaining 30 % is gradually formed with a time constant of 290 ps. Such a rapid formation of Pe radical cation is consistent with no change in the fluorescence decay in the SPC measurement. The Pe radical cation formed by the one-photon excitation rapidly decays and disappears in less than microseconds, while the radical cations formed by photoionization is stable enough to be detected by steady-state absorption

spectroscopy because electrons are ejected several nm away from the parent radical cation [21]. If the rapid one-photon quenching competes with the multi-photon ionization, the radical cation yield by multi-photon ionization should decrease at higher TCNB concentrations. As mentioned above, however, no change in the radical cation yields is observed even at higher TCNB concentrations. Therefore, we conclude that the relaxed singlet excited state of Pe is not involved in the photoionization with ps and fs lasers; in other words, simultaneous multi-photon ionization rapidly occurs in competition with the static quenching in the excited state. (Scheme 1b). This mechanism can be mainly ascribed to the pulse excitation as short as the vibrational relaxation time of aromatic molecules. Thus, we speculate that similar mechanism would basically work for other aromatic molecules studied here, although further experiments are required to address each mechanism in detail.

4. Conclusions

We have studied the multi-photon ionization of aromatic molecules in PMMA solids, in which more than two photons are involved, with ps and fs lasers. Radical cations of Pe, 3T, TMB, TMPD, and EtCz were formed in PMMA solids through resonant two-photon ionization with a 355-nm ps laser. On the contrary, the same radical cations were produced by the indirect excitation at 800 nm as well as the direct excitation at 400 nm. The former is ascribed to resonance-enhanced multi-photon ionization, while the latter to resonant two-photon ionization. In either case, the lowest singlet excited state contributes directly or indirectly to the ionization as an intermediate state depending on the optical gap. The photoionization yields of Pe with ps and fs lasers are independent of the concentration of TCNB that efficiently quenches the excited state within 100 fs. Therefore, we conclude that the cation formation by ps and fs laser excitation is due to essentially simultaneous multi-

photon ionization through non-relaxed excited states as an intermediate rather than step-wise multi-photon ionization.

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Figure Captions

Fig. 1. Normalized absorption spectra of various radical cations formed in a PMMA block at room temperature by photoionization of dopant aromatic molecules with 355-nm Nd:YAG ps laser ($\sim 5 \times 10^8 \text{ W cm}^{-2}$, 10 Hz,): Pe radical cation (—), 3T radical cation (---), EtCz radical cation (••••), TMB radical cation (-•-•-), TMPD radical cation (-••-••-).

Fig. 2. Absorption spectra of the Pe (solid lines) and EtCz (broken lines) radical cations formed in a PMMA block at room temperature by photoionization of dopant aromatic molecules with Ti:sapphire fs laser, 10 Hz, 10000 shots: a) 400 nm ($\sim 5 \times 10^9 \text{ W cm}^{-2}$) and b) 800 nm ($\sim 10^{11} \text{ W cm}^{-2}$).

Fig. 3. Yields of Pe radical cation (open circles and triangles) and TCNB radical anion (closed circles and triangles) plotted against TCNB concentration at room temperature by photoirradiation of Pe molecules with a) 355-nm ps laser (circles, $\sim 5 \times 10^8 \text{ W cm}^{-2}$, 10 Hz,) and b) 400-nm fs laser (triangles, $\sim 5 \times 10^9 \text{ W cm}^{-2}$, 10 Hz). Experimental errors are estimated to be $\pm 5 \%$.

Fig. 4. a) Fluorescence spectra of Pe doped in PMMA films with TCNB acceptor at room temperature: [TCNB] = 0 to 40 mM from top to bottom. Fluorescence intensity is corrected by the absorbance of Pe at an excitation wavelength of 400 nm. b) Fluorescence decay curves of Pe doped in PMMA films with TCNB acceptor at room temperature: [TCNB] = 0 to 40 mM from top to bottom. The excitation and monitor wavelengths were 410 and 470 nm, respectively. The broken line shows an excitation laser pulse.

Fig. 5. a) Femtosecond transient absorption spectra of PMMA blocks doped with Pe (0.2 mM) (broken line) and doped with Pe (0.2 mM) and TCNB (40 mM) (solid line) at 0 ps excited at 400 nm with an excitation intensity of $\sim 10^7 \text{ W cm}^{-2}$. The dotted line represents the steady-state absorption spectrum of Pe radical cation formed in a PMMA block. b) Time evolution of transient absorption at 550 nm measured for a PMMA block doped with Pe (0.2 mM) and TCNB (40 mM) excited at 400 nm with an excitation intensity of $\sim 10^7 \text{ W cm}^{-2}$. The broken line represents the best-fit curve.

Scheme 1. Schematic energy diagrams: a) static quenching of the excited state of Pe formed by one-photon excitation, b) simultaneous ionization of Pe by two-photon excitation.

Table 1

Ionization potentials of aromatic molecules in the gas phase and in a PMMA solid, and polarization energies of the radical cations in a PMMA solid calculated by the Born equation ^a

	IP_g / eV^b	IP_s / eV^c	r_+ / nm^d	P_+ / eV^e
Pe	6.9 [13]	5.9	0.38	-1.0
3T	7.4 [14]	6.3	0.36	-1.1
EtCz	7.7 [15,16]	6.6	0.36	-1.1
TMB	6.5 [17]	5.5	0.39	-1.0
TMPD	6.7 [18]	5.6	0.35	-1.1

^a See Eqs. (1) and (2).

^b IP_g : Ionization potential of aromatic molecules in the gas phase.

^c IP_s : Ionization potential of aromatic molecules in a PMMA solid.

^d r_+ : Radius of these radical cations.

^e P_+ : Polarization energy of these radical cations in a PMMA solid.

Table 2

Formation of radical cations of aromatic molecules in a PMMA solid by photo-irradiation ^a

Intensity / W cm ⁻²	ps laser			fs laser	
	355 nm	532 nm	1064 nm	400 nm	800 nm
	5×10^8	5×10^8	2.5×10^8	5×10^9	$\sim 10^{11}$
Pe	Y	N	N	Y	Y ^b
3T	Y	N	N	Y	Y ^b
EtCz	Y	N	N	Y	Y ^c
TMB	Y	N	N	Y	Y ^c
TMPD	Y	N	N	Y	Y ^c

^a Y: Formation of radical cations; N: No formation of radical cations. The condition of photo-irradiation was 10 Hz and 10000 shots.

^b 8×10^{10} W cm⁻².

^c 3.2×10^{11} W cm⁻².

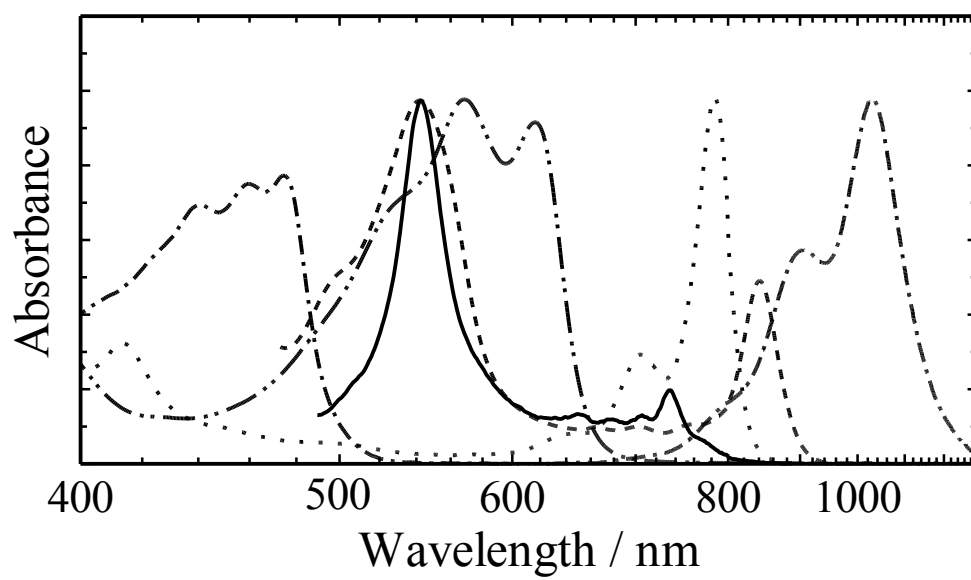


Fig. 1. J. Guo et al.

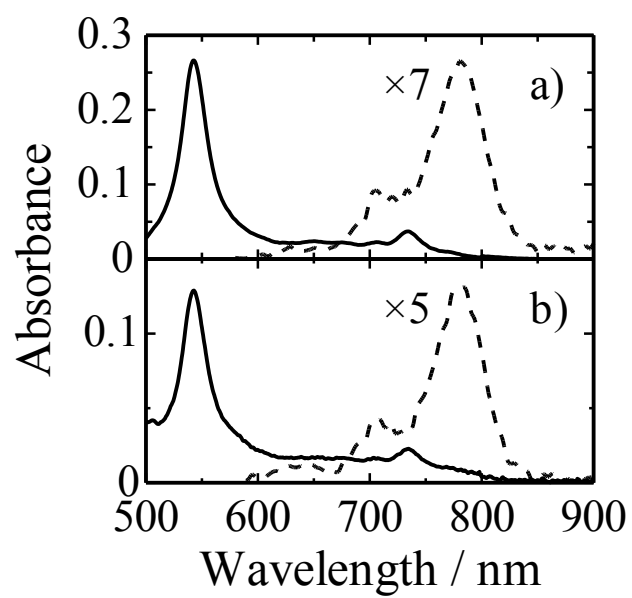


Fig. 2. J. Guo et al.

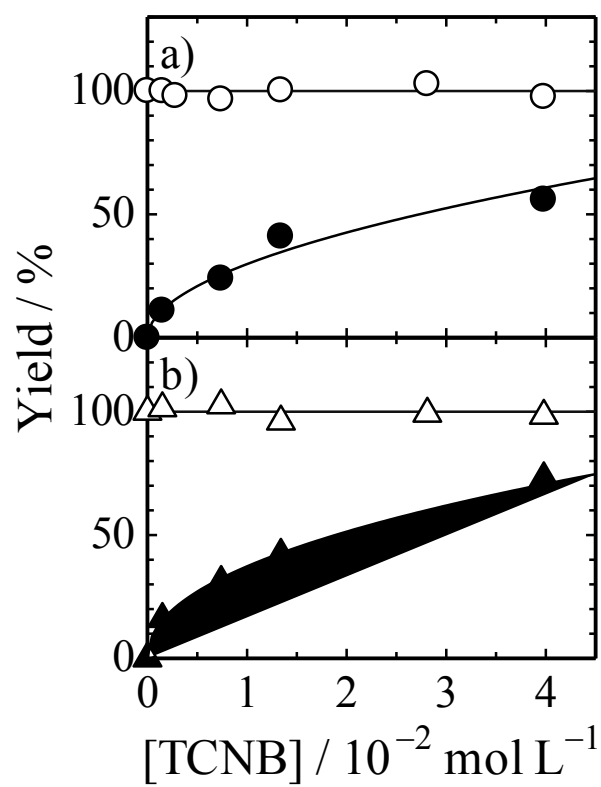


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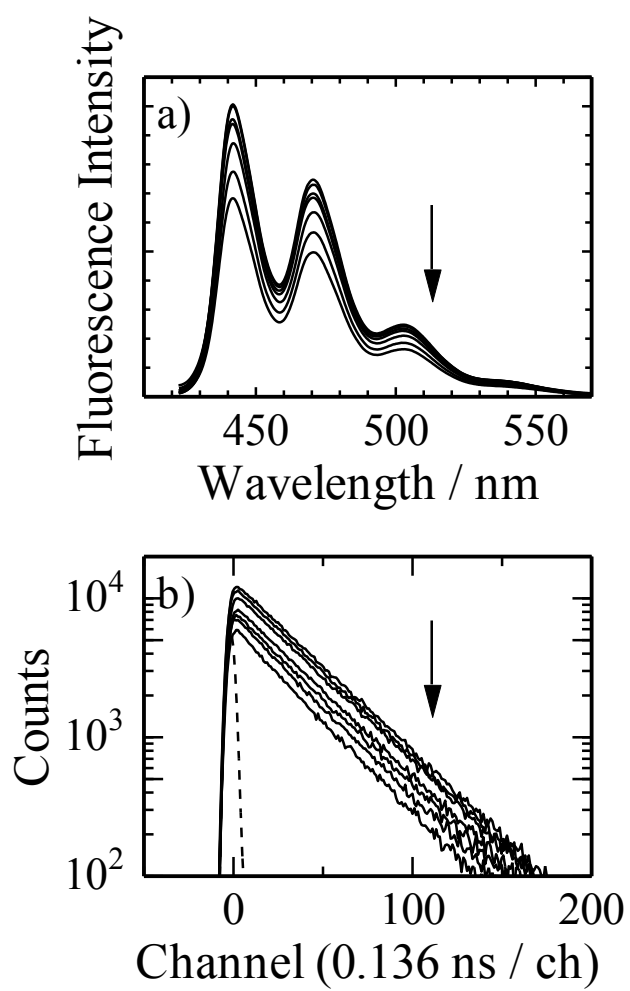


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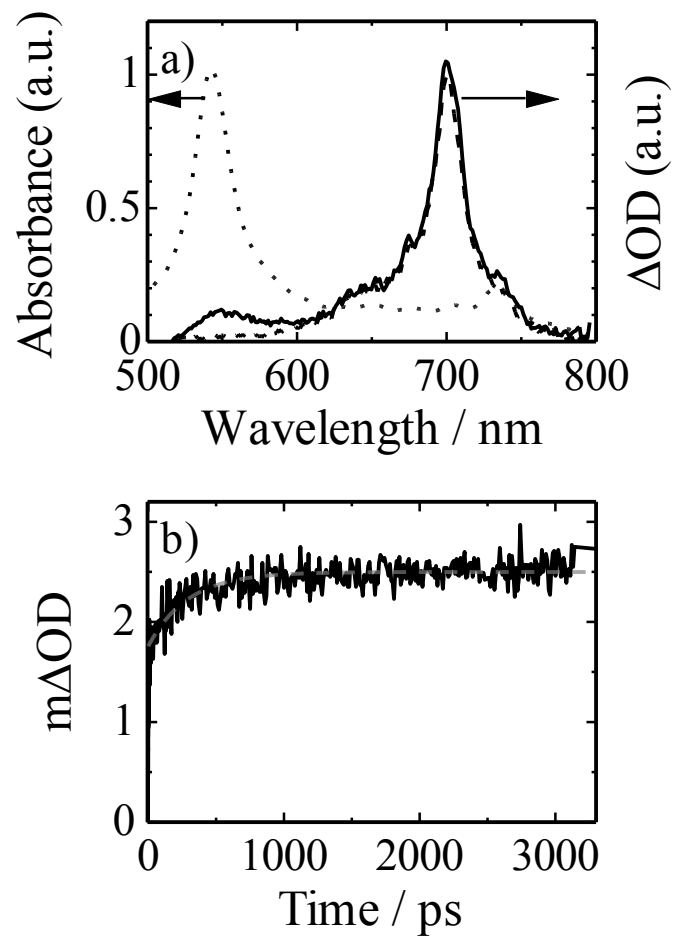
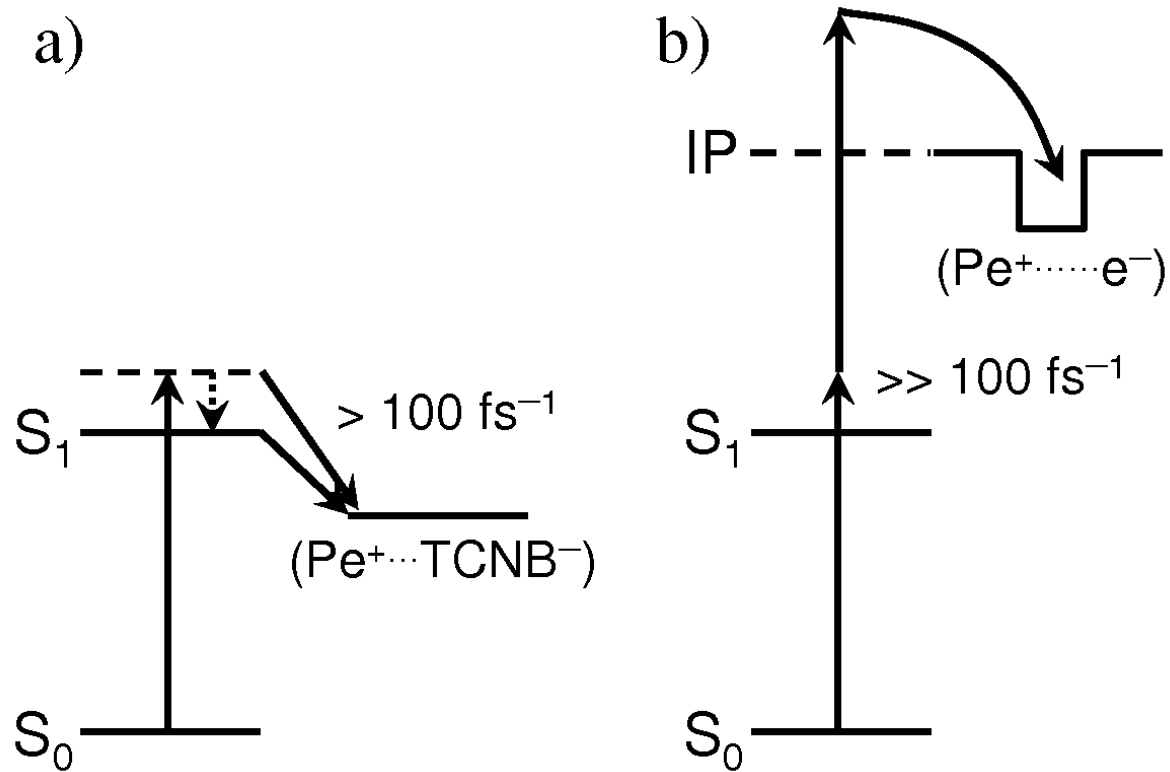


Fig. 5. J. Guo et al.



Scheme 1. J. Guo et al.

Graphical abstract

Multi-photon ionization of aromatic molecules in PMMA solids is discussed on the basis of electron scavenging and time-resolved spectroscopic experiments.

