

Large resonant third-order optical nonlinearity of thin film containing J-like aggregates of a *bis*[4-(*N*-dibutylamino)phenyl]squarylium dye

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Abstract. The third-order optical nonlinearity and response of thin film containing J-like aggregates of a *bis*[4-(*N*-dibutylamino)phenyl]squarylium dye were measured by degenerate four-wave mixing (DFWM) technique under resonant conditions. The temporal profile of DFWM signal was obtained with a time resolution of 0.3 ps (FWHM), and was found to consist of at least two components, i.e. the coherent instantaneous nonlinear response (electronic response) and the slow response due to the excited state population grating. The effective $\chi^{(3)}$ value of thin squarylium dye film was evaluated to be as high as 1.1×10^{-7} esu, and the figure of merit of third-order nonlinearity $F (F = \chi^{(3)}/\alpha)$, was calculated to be about 2.1×10^{-13} esu cm.

Keywords. Degenerate four-wave mixing; J-like aggregates; third-order nonlinear susceptibility; squarylium dye.

1. Introduction

Nonlinear optical films with large optical nonlinearity and ultrafast response are required as promising candidates for future integrated photonics applications, such as all-optical switching, dynamic holography, data storage, optical communication, etc (Norwood and Sounik 1992; Nalwa 1993; Liu *et al* 2008; Hou *et al* 2010; Chen *et al* 2011; Sabari Girisun *et al* 2011). Among optical materials, aggregates of organic dyes are ordered molecular assemblies with mesoscopic size and are different from molecular crystals due to their specific optical properties. Cyanine dyes can readily form large aggregated structures that consist of several tens to hundreds of molecular units either by electrostatic or van der Waals interaction. This phenomenon has been observed as early as in the 1930s by Jelley (1936) and Scheibe (1937). The corresponding type of molecular aggregates is referred to as J-aggregates. The most characteristic feature of J-aggregates is that they exhibit a narrow peak (J-band) red-shifted in the absorption spectrum with respect to the monomer absorption.

Because of the resonant dipole–dipole interaction between adjacent molecules and the translational symmetry of the system, absorption of a photon produces a coherent delocalized excitation or exciton in the J-aggregates. An exciton involves a collective oscillation of N adjacent dipoles in a chain or in a lattice of molecules, leading to an N -fold enhancement of

the transition oscillator strength and a corresponding increase in the probability of absorption and emission of light. In the J-aggregates, high oscillator strength value manifests itself as a drastic shortening of the spontaneous radiative decay time (Boer and Wiersma 1990). The lifetime of the exciton can be further reduced by an exciton–exciton annihilation process, resulting in a picosecond or sub-picosecond relaxation rate. On the other hand, high oscillator strength also provides an increased resonant nonlinear susceptibility value (Spano and Mukamel 1989a). In the present study, we found that *bis*[4-(*N*-dibutylamino)phenyl]squarylium dye forms J-like aggregates in thin film, and the third-order nonlinear optical property of J-like aggregates of this squarylium dye was measured by the femtosecond degenerate four-wave mixing (DFWM) technique under resonant conditions.

2. Experimental

The *bis*[4-(*N*-dibutylamino)phenyl]squarylium dye (structural formula as shown in figure 1) was synthesized in accordance with a reported procedure (Sprenger and Ziegenbein 1966). Film of the squarylium dye J-like aggregates was formed on glass substrates by the spin-coating method from a solution of *bis*[4-(*N*-dibutylamino)phenyl]squarylium dye at a concentration of 1.0 wt% dissolved in 1,2-dichloroethane. The film has high optical qualities with good optical transparency, excellent homogeneity and optical stability.

Film thickness was determined to be about 100 nm using a surface profiler (ULVAC, Dektak³). All the absorption

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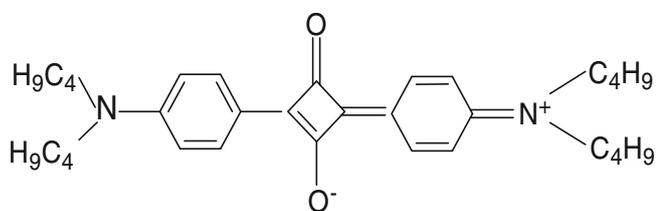


Figure 1. Structural formula of bis[4-(*N*-dibutylamino)phenyl]squarylium dye.

spectra of samples were recorded with a Jasco V-550 spectrophotometer. Time-resolved fluorescence lifetime measurements were carried out using a combination of a Ti:sapphire laser (Spectra Physics, Tsunami) and a streak camera (Hamamatsu, Streak Scope C4334).

The third-order nonlinear optical property of the sample was measured using the forward DFWM technique. The system used in our experimental study of DFWM is the same as that described in previous papers (Li *et al* 2005a,b). The folded box-CARS type geometry with three linearly polarized beams of the fundamental output of a Ti:sapphire regenerative amplifier laser (Spectra-Physics, Spitfire, 130 fs, 1 kHz, 1 W) was used for DFWM experiment. Two of the three forward beams are used for the generation of a refractive index grating in sample, while the third beam is used for the detection of this grating, i.e. the light-induced change of the refractive index. The wavelength of the laser was adjusted to 760 nm. The laser beam was largely attenuated by ND filters in order to avoid saturation. The energies of beams 1 and 2 were < 100 nJ/pulse and that of beam 3 was < 10 nJ/pulse. The intensity of the laser radiation on samples was about 1 GW/cm². The sample was simultaneously irradiated with beams 1 and 2, and then irradiated with beam 3 after a suitable delay time. The three collinear beams were focused onto the sample by a lens with a 500 mm focal length. Beam 4, the produced DFWM signal, was detected by a CCD after passing through a monochromator. The output of CCD was acquired using a personal computer. The time resolution of the system was ca. 0.3 ps (FWHM). The intensity of DFWM signal due to the solvent and quartz cuvette was completely negligible. The experimental uncertainty was estimated to be within $\pm 20\%$.

The effective third-order nonlinear susceptibility, $\chi^{(3)}$, was calculated by comparison with the signal of a reference sample, CCl₄ ($\chi^{(3)} = 4.01 \times 10^{-14}$ esu) (Kamada *et al* 1996) measured under the same conditions, and was corrected for the absorption losses according to the following relationship

$$\chi_{\text{sample}}^{(3)} = (n_{\text{sample}}/n_{\text{ref}})^2 (I_{\text{sample}}/I_{\text{ref}})^{1/2} (L_{\text{ref}}/L_{\text{sample}}) \times \alpha L_{\text{sample}} \exp(\alpha L_{\text{sample}}/2) \times [1 - \exp(-\alpha L_{\text{sample}})]^{-1} \chi_{\text{ref}}^{(3)}, \quad (1)$$

where I is the DFWM signal intensity, α the linear absorption coefficient, n the refractive index and L the interaction

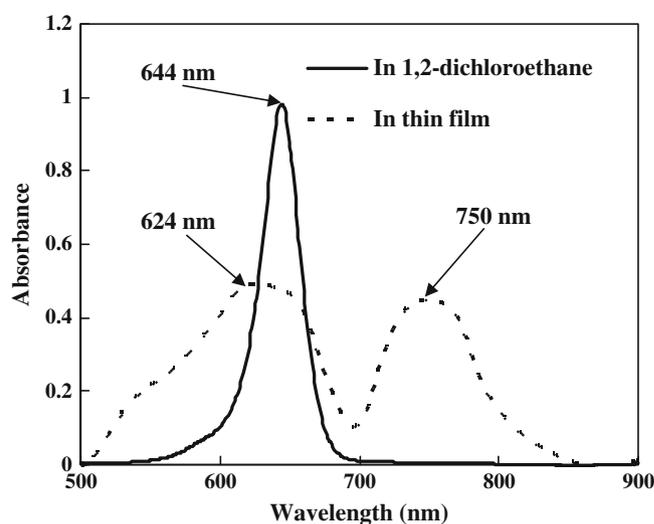


Figure 2. Absorption spectra of bis[4-(*N*-dibutylamino)phenyl]squarylium dye in dilute 1,2-dichloroethane solution (solid line) and in a thin film (dotted line).

length. The subscript 'ref' refers to the reference. Instead of using CS₂, we used CCl₄ as a reference. The reason is that the molecular anisotropy of CS₂ makes it undergo molecular reorientation under the action of laser pulses and give rise to orientation nonlinearity. The rise and fall times for this orientational contribution to DFWM signal are 200 and >600 fs, respectively (Ruhman *et al* 1987; McMorrow *et al* 1988). Therefore, it is not appropriate in femtosecond regime to use the known effective $\chi^{(3)}$ value of CS₂ as reference to evaluate the effective $\chi^{(3)}$ value of sample. On the other hand, isotropic structure of CCl₄ and its instantaneous response makes CCl₄ an excellent reference material for femtosecond DFWM.

3. Results and discussion

Figure 2 shows absorption spectra of bis[4-(*N*-dibutylamino)phenyl]squarylium dye in dilute 1,2-dichloroethane solution (solid line) and in a thin film (dotted line). The squarylium dye in 1,2-dichloroethane dilute solution exhibits intense absorption in the visible region with absorption maximum at 644 nm. The large extinction coefficient and narrow bandwidth are consistent with the donor–acceptor–donor (D–A–D) electron transfer character of the $S_0 \rightarrow S_1$ absorption (Bigelow and Freund 1986). It can be seen that the absorption spectrum of the squarylium dye thin film is much broader, which has a longer maximum wavelength at 750 nm and a blue-shift absorption band at 624 nm compared to that of 1,2-dichloroethane solution. Drobizhev *et al* (2000) attributed H-band (H-aggregates) to the upper Davydov component and J-band (J-aggregates) to lower Davydov component. The absorption of the J-aggregates was influenced by size of the aggregate, interfacial distance between the neighbouring dyes and slipping angle of the stacked dyes (Miyata *et al* 1993;

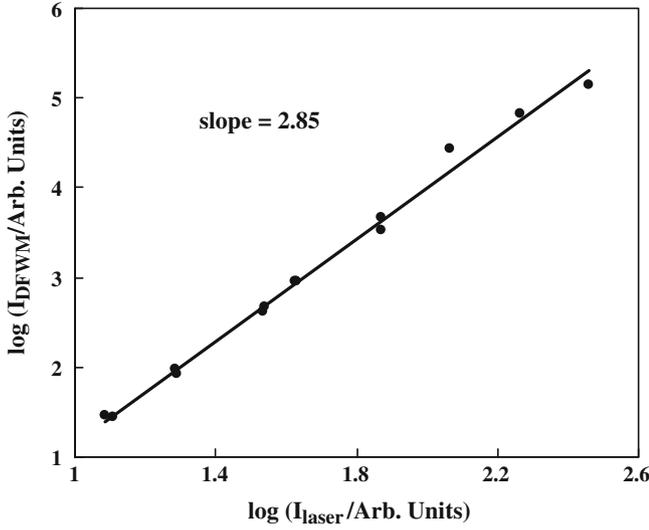


Figure 3. Dependence of DFWM signal intensity of J-like aggregates of *bis*[4-(*N*-dibutylamino)phenyl]squarylium dye on input laser power.

Sayama *et al* 2002). The static and dynamic disorder (a wide distribution of different arrangements) of the dye molecules on the glass substrate probably caused broad absorption spectra. We refer to the aggregates showing a broad absorption at a longer wavelength region as J-like aggregates mentioned below. Therefore, the appeared red-shift and broad band can be attributed to the formation of J-like aggregates of *bis*[4-(*N*-dibutylamino)phenyl]squarylium dye molecules.

Figure 3 shows a log-log plot of DFWM signal intensity against pump beam intensity for the thin film containing squarylium dye J-like aggregates. The plot has a slope at nearly around 3 indicating a third-order nature of the process. This also shows that there is no saturation of optical nonlinearity under the measured conditions. The temporal profiles of DFWM signal were measured as a function of delay time of beam 3. The result is shown in figure 4. Each temporal profile has at least two components, a rapidly decaying component and a slow component. The fast component is primarily determined by the laser pulse, and can be attributed to the contribution from the electronic response. The slow component appears to be associated with the excited state population grating.

To analyse the temporal profile of a DFWM signal of *bis*[4-(*N*-dibutylamino)phenyl]squarylium dye film, it was simulated. The observed DFWM temporal profile, $I(t)$ is assumed to be expressed by the following convolution integral

$$I(t) = \int_0^t L(t') R(t-t') dt', \quad (2)$$

where $L(t)$ is the temporal profile of the laser and $R(t)$ the DFWM response of sample irradiated by a laser with an

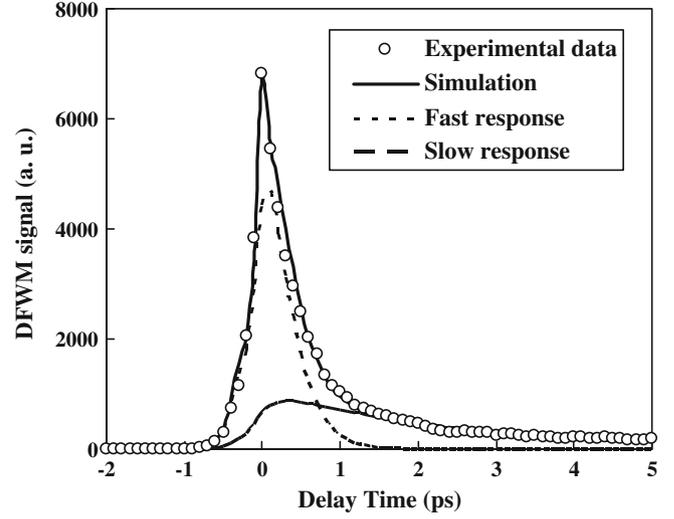


Figure 4. Simulation for a temporal profile of DFWM signal of squarylium dye film by assuming Förster type energy transfer; open circles, solid line, dotted line and broken line represent experimental data, simulation, fast component and slow component, respectively.

ideal delta function shape pulse. $R(t)$ is assumed to be a biexponential function

$$R(t) = \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2). \quad (3)$$

The slow response of a DFWM signal of the squarylium dye film was not exponential. The excited monomer will be quenched by dimer or aggregates. Förster's (1949) theory states that the temporal behaviour of the concentration of excited donor molecules quenched by energy acceptor molecules randomly distributed in a three-dimensional space can be expressed by the following equation

$$\rho(t) = \exp\left[-t/\tau_D - \gamma_A (t/\tau_D)^{1/2}\right], \quad (4)$$

where τ_D is the lifetime of the donor without an acceptor and γ_A is a constant related to energy transfer rate.

DFWM signal intensity of a population grating is proportional to the square of the concentration of excited molecules. Therefore, $R(t)$ for the squarylium dye J-like aggregates film can be assumed to be the sum of an exponential function (electronic component) and a slow response (population grating) and expressed as follows

$$\begin{aligned} R(t) &= \alpha_1 \exp(-t/\tau_1) + \alpha_2 \rho(t)^2 \\ &= \alpha_1 \exp(-t/\tau_1) \\ &\quad + \alpha_2 \exp\left[-2t/\tau_D - 2\gamma_A (t/\tau_D)^{1/2}\right]. \end{aligned} \quad (5)$$

All the parameters in (4) and (5), the time difference between the experimental and simulated DFWM temporal profile, Δt , were determined using a nonlinear, least-squares iterative convolution method based on the Marquardt algorithm (Marquardt 1963; O'Connor *et al* 1979). DFWM temporal profile of a glass plate is used as $L(t)$.

Figure 4 shows simulation of temporal profiles for DFWM signal of thin film containing J-like aggregates of the squarylium dye (solid line), which were simulated in accordance with above referred method by a biexponential function and assuming Förster type energy transfer. It was found that the simulated curve reproduced the experimental values very well. The observed decay of DFWM signal consists of at least two components, i.e. fast component induced by the contribution from the coherent instantaneous nonlinear response (electronic response) and slow component due to the contribution from the population grating of excited state. The fast component has a decay time constant shorter than 0.06 ps, which is primarily determined by the laser pulse, and the slow component has a decay time constant of ca. 7.6 ps. Based on simulation, percentage of the slow component is about 23%. Therefore, the contribution from the fast component becomes dominant for the DFWM signal of the squarylium dye film because of aggregation effect on DFWM response.

The time-resolved fluorescence of *bis*[4-(*N*-dibutylamino)phenyl]squarylium dye thin film is shown in figure 5. It was found that the fluorescence lifetime of the squarylium dye in film is very short and the fluorescence intensity is very weak, which indicates that nonradiative processes are dominant in squarylium dye thin film. Sakakibara *et al* (2001) reported that solid films of magnesium, chloroaluminum, and metal-free phthalocyanines have much smaller fluorescence quantum yields than the corresponding monomers due to large intermolecular interactions. Within nonradiative decay processes, exciton coupling and energy transfer between squarylium dye molecules probably account for the fast decay of the S_1 state. We considered that, for the squarylium dye film, which primarily consists of J-like aggregates, energy transfer from site to site within the J-like aggregates gives rise to the shortening of the S_1 state lifetime.

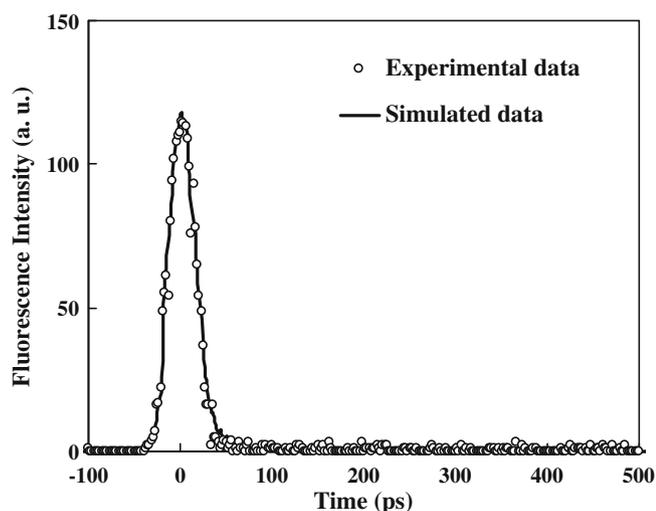


Figure 5. Time-resolved fluorescence of *bis*[4-(*N*-dibutylamino)phenyl]squarylium dye thin film.

We evaluated the electronic component of the third-order nonlinear optical susceptibility, $\chi^{(3)}$, by putting the intensity of the fast component calculated by the corresponding simulation into (1) as I_{sample} . The obtained $\chi^{(3)}$ value is about 1.1×10^{-7} esu at 760 nm. This large third-order nonlinear optical susceptibility can be considered to be induced from the J-like aggregates of squarylium dye formed in the film. Furthermore, the figure of merit of third-order nonlinearity, F ($F = \chi^{(3)}/\alpha$), was evaluated to be about 2.1×10^{-13} esu cm.

Previous experimental and theoretical works have shown that molecular J-aggregates are self-organized systems that combine a strong third-order optical susceptibility in the exciton absorption band (J-band) with a short response time (Spano and Mukamel 1989b; Kobayashi and Sasaki 1994; Markov *et al* 2000; Zhou *et al* 2000; Tatsuura *et al* 2001). The large optical properties of J-aggregates derive from the delocalization of the Frenkel excitons over many molecules of the aggregate. For perfectly ordered (homogeneous) aggregates the exciton wave functions are entirely delocalized and the delocalization length, N_{del} , is determined by the physical size of aggregates, $N_{\text{del}} = N$. In practice, however, the aggregates contain some amount of disorder, which may severely affect the delocalization behaviour and observed optical properties. Disorder can either be diagonal, meaning a spread in transition frequencies of individual molecules, or off-diagonal, expressing a variation in the intermolecular interactions. Diagonal disorder corresponds to the situation of inhomogeneous broadening due to different molecular surroundings. Off-diagonal or interaction disorder, on the other hand, implies physical irregularity of chain itself. This irregularity can exist in the positions and (or) orientations of the molecules (Fidder *et al* 1991). As a result, the exciton wave functions localize on a part of the aggregate, with a delocalization length which may be smaller than the physical size of aggregates. A supralinear scaling of the cubic optical nonlinearity, $\chi^{(3)}$, with the exciton delocalization size (so-called size-enhancement) has been theoretically predicted for ordered aggregates as well as for aggregates with static diagonal disorder (Knoester 2003). Markov *et al* (2003) studied the nanometer films of J-aggregates of pseudoisocyanine (PIC) with various degrees of both static and dynamic disorder, and established the scaling of the nonlinear optical susceptibility per aggregate molecule, $\chi^{(3)}/N$, with the delocalization length as $\chi^{(3)}/N \propto N_{\text{Del}}^{\gamma}$, with $\gamma = 2.3 \pm 0.2$. This power scaling agrees very well with the theoretical prediction of $\gamma = 2.36$ for the size-enhancement in one-dimensional aggregates with static diagonal disorder (Knoester 2003). In the present study, considering the J-like aggregates of squarylium dye embedded in a glass environment, the absorption line broadening arising from the interactions with environment should be taken into account. Assuming that the linewidth of the exciton absorption line is dominated by static disorder, static disorder reduces the delocalization of excitation over an aggregate to some amount (exciton delocalization length) of molecular units.

A few resonant $\chi^{(3)}$ values of the J-aggregates of dyes have been reported. For example, the J-aggregates of a

PIC-Br in LB film ($\chi^{(3)} = 5 \times 10^{-7}$ esu) (Zhou *et al* 2000), and Markov *et al* (2003) reported the nonlinear optical properties of the J-aggregates of PIC iodide with several different *N*-alkyl substituents by the *Z*-scan technique, a giant third-order optical nonlinearity ($\chi^{(3)} \approx 10^{-5}$ esu) (Markov *et al* 2000) was obtained. Because they used a nanosecond pulsed dye laser, we thought that there were contributions to third-order optical nonlinearity from slow responses such as population gratings and thermal gratings. In the present study, we only determined the contribution of electronic response of the $\chi^{(3)}$ for the thin film. Though the absorption band of the J-like aggregates of bis[4-(*N*-dibutylamino)phenyl]squarylium dye is a little broader than those of above mentioned J-aggregates, thin film containing bis[4-(*N*-dibutylamino)phenyl]squarylium dye J-like aggregates also show very large third-order optical nonlinearity.

To put in perspective the merits of the studied squarylium dye, we have tried to compare its third-order optical nonlinearity with some of the other molecules reported recently. Kumar *et al* (2009) measured off-resonant nonlinearities of alkyl phthalocyanines in the range of $\sim 10^{-31}$ esu with fast response times (< 100 fs). Our group (Li *et al* 2007a) presented previously the results on centrosymmetric squaraines possessing large third-order optical nonlinearities studied using femtosecond DFWM technique and achieved γ values of $\sim 10^{-31}$ esu. We also reported similar studies on novel diarylethene-phthalocyanine dyads with largest γ value for one of the compounds being $\sim 10^{-30}$ esu (Li *et al* 2007b). Prabhakar *et al* (2008) presented their results of croconate dyes obtained with 100 fs pulses where off-resonant γ value was found to be $\sim 10^{-32}$ esu. Furthermore, they also reported recently third-order optical nonlinearities of centrosymmetric squaraine derivatives using femtosecond DFWM technique at 800 nm, the γ values, though smaller than the squaraine dye having absorption in the red region, are reasonably large and range from -1.2 to -6.9×10^{-33} esu (Prabhakar *et al* 2010). In our present study, thin film containing J-like aggregates of bis[4-(*N*-dibutylamino)phenyl]squarylium dye shows large third-order nonlinear susceptibility due to resonance enhancement and J-aggregation effect. Though the off-resonant third-order optical nonlinearity of studied squarylium dye in solution has not been measured, we think the γ value should also be reasonably large because of significant intramolecular charge transfer (ICT) of squaraine molecules (Dirk *et al* 1992).

4. Conclusions

The magnitude and dynamic response of the third-order optical nonlinearity of J-like aggregates of bis[4-(*N*-dibutylamino)phenyl]squarylium dye were measured by femtosecond DFWM technique under resonant condition. Time-resolved DFWM measurement indicates that the J-like aggregates of bis[4-(*N*-dibutylamino)phenyl]squarylium dye

shows fast nonlinear optical response and large third-order nonlinear susceptibility. The effective $\chi^{(3)}$ value of the J-like aggregates of bis[4-(*N*-dibutylamino)phenyl]squarylium dye was evaluated to be as high as 1.1×10^{-7} esu, and the figure of merit of $\chi^{(3)}/\alpha$ was calculated to be about 2.1×10^{-13} esu cm. The present squarylium dye has significant potential for applications in third-order nonlinear optics.

Acknowledgements

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