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Photophysics on Solid Surfaces. Time-Resolved Fluorescence Spectra of Pyrene Adsorbed on Calcinated Vycor Glass

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The fluorescence, fluorescence excitation, and time-resolved fluorescence spectra of pyrene molecules adsorbed on calcinated (773 K) Vycor glass (average pore diameter, 40 Å) have been investigated as a function of the amount of adsorbed pyrene. The results of the analyses of these spectra and multi-component decays of fluorescence suggest that there are three fluorescent species with different decay times on the surface of Vycor glass. Their lifetimes are determined to be 303—355, 100—145, and 19—48 ns. These decay components are reasonably assigned to the emissions of monomeric, dimeric, and excimer-like species in the order of decreasing the lifetimes. A 26600 cm^{-1} peak appearing at the first stage of the time-resolved fluorescence spectra is assingned to the 0—0 hand of dimeric pyrene based on the results reported by Yamazaki et al. in the Langmuir-Blodgett monolayer.

The photochemistry and photophysics on solid surfaces and in adsorbed layers have recently been given considerable attention in connection with the most promising subjects to functionalize solid surfaces as well as with better understanding of the properties of solid surface itself.[1—4] Many workers have paid attention to the photophysics of pyrene adsorbed on solid surfaces such as silica gel, activated alumina, and Vycor glass, because pyrene has a relatively long fluorescence lifetime and its photophysical properties are sensitive to the nature of the environment such as polarity.[5—21]

It has been reported that pyrene molecules adsorbed on silica gel[10—15,19,20] and zeolite[16,21] form a ground-state dimer in the pore of the adsorbents. The weakly bound ground-state bimolecular association seems to be one of the most specific features in the adsorbed layer, its extent depending on the concentration of adsorbed molecules as well as the chemical and physical nature of the adsorbents. The formation of excimer-like pyrene is much easier on the solid surface than in solution where the rate of the formation of excimer is diffusion-controlled.[22] The formation of dimeric pyrene is a consequence of surface interaction since pyrene does not associate in solution in its ground state due to a repulsive potential between two unexcited molecules.[22]

Picosecond time-resolved fluorescence spectra of pyrene molecules in the Langmuir–Blodgett monolayer film (LB-film) have revealed that fluorescence from dimeric pyrene is a dominant component in the initial time region (0—100 ps) and its 0-0 band appears at 381 nm (26250 cm^{-1}), being red-shifted by 280 cm^{-1} (4 nm) compared with that of monomer at 377 nm (26530 cm^{-1}).[17,18] Recently the dimer conformation and fluorescence quantum yields of pyrene molecules on silica gel have been studied as a function of the amount of adsorbed pyrene by means of steady-state fluorescence measurements.[19,20] All these experimental results indicate that adsorbed pyrene molecules mainly exist in the monomeric and dimeric(or ground-state aggregates) forms on the surfaces of solid including porous Vycor glass.

It is worthwhile to elucidate photophysical processes of adsorbed molecules in terms of a distribution of various sites since the surface of Vycor glass is inhomogeneous in nature.[23,24] Experimental findings, however, show that adsorbed dimeric pyrene molecules on solid surfaces have a definite geometry.[10—16, 19] We therefore confine our attention to the chemical species on solid surfaces. A preceding paper reported the results of fluorescence spectra of pyrene adsorbed on porous Vycor glass with a surface coverage of 0.0014 (34 μg/g-Vycor).[25] The present work reports the detailed results of the analyses of the fluorescence and fluorescence-excitation spectra, time-resolved fluorescence spectra, and the multi-component fluorescence decay curves of pyrene molecules adsorbed on calcinated (773 K) Vycor glass, by comparing the present results with those obtained on solid surfaces and LB film.

Experimental

Pyrene (Wako Pure Chemical Industries, Inc., reagent grade) was purified by repeated recrystallizations from ethanol solution and passed 230 times through a zone refiner. Cyclohexane (Wako, Luminasol grade) was used without further purification. Porous Vycor glass (Vycor) (Corning code No. 7930, major composition: $SiO_2 > 96\%$; $B_2O_3 > 3\%$, BET surface area: 155 m^2 g^{-1}, average pore diameter: 40 Å) was used as an adsorbent. Prior to experiments, a (1×5×20) mm^3 sheet of Vycor glass was placed in a quartz cell and then evacuated in vacuo (less than 1×10^{-5} Torr, 1 Torr=133.322 Pa) at 773 K for 5 h. Adsorption of pyrene molecules onto Vycor glass was carried out by pouring degassed cyclohexane solution into the quartz cell in which pretreated Vycor glass was placed in vacuo at 295 K. The used cyclohexane solutions were subjected to 5—6 cycles of freeze-pump-thaw to remove oxygen before the adsorption procedure. After the impregnation the supernatant solution was removed by decantation and then evacuated in vacuo for 5 h at 373 K.[26] The quartz cells were sealed under vacuum, and these samples were used for steady-state luminescence and lifetime measurements.

The amount of pyrene adsorbed on Vycor glass was determined to be 34 μg/(g-Vycor) to 5.7 mg/(g-Vycor) by measuring the adsorption spectra of the supernatant solution. Hereafter the amount of adsorbed pyrene (x mg(or μg)) onto 1 g of porous Vycor glass is represented by x mg(or μg) g.$^{-1}$ The amount of pyrene required for 100% surface coverage is 25 mg assuming that an adsorbed pyrene molecule occupies a surface area of 150 Å^2.[11,12,19] Therefore, the surface coverage of pyrene is to be 0.001—0.21.[27]

It is known that the species on surface of Vycor glass are the physisorbed and chemisorbed H_2O and the various types of surface hydroxyl groups such as Si-OH and B-OH.[28—31] After the treatment in vacuo at 773 K, the presence of physisorbed H_2O might be negligible and the H_2O only remains as the surface hydroxyl groups. The residual numbers of hydroxyl groups under the conditions are 1—3 groups/nm^2.[30,31] Adsorption and emission spectra were recorded on a Hitachi 220 recording spectrophotometer and a Hitachi F-3000 fluorescence spectrophotometer, respectively. Both excitation and emission spectra were measured by a front-face excitation geometry. Measurements of fluorescence decay and time-resolved fluorescence spectra were carried out by using a single-photon fluorescence lifetime instrument.[32] A nitrogen lamp firing at ca. 10,000 pulse per second served as the excitation source. The wavenumber, 29660 cm^{-1}, was used as the excitation light and the full-width at half-maximum is 2.5 ns. A NAIG(Model E-562) process memory and an NEC-9801 personal computer were used for data collection, storage, and manipulation. The fluorescence lifetimes obtained by the instrument were found to agree well with widely accepted literature values.[33]

Results and Discussion

Fluorescence and Fluorescence-Excitation Spectra. Figure 1 shows the fluorescence spectra of pyrene adsorbed on Vycor glass with the amounts of 34 μg g^{-1}, 1.2 mg g^{-1} and 5.7 mg g^{-1} at 295 K. The excitation wavenumber corresponds to the ^1L_b transition of pyrene. It is easily seen that the entire fluorescence are composed of the monomer-like emission(FM) at higher wavenumber around 25000 cm^{-1} and the excimer-like emission(FE) at lower wavenumber around 21000 cm^{-1}. The fluorescence spectra of pyrene adsorbed on Vycor glass with the lowest surface coverage mainly consists of FM emission, showing a sharp and structured vibrational fine structure at around 24000—26000 cm^{-1}.

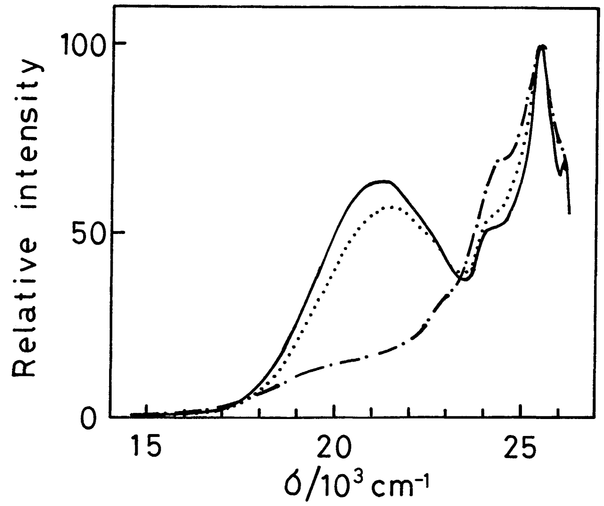

Fig. 1. The dependence of the fluorescence spectra of pyrene on the amount of pyrene adsorbed onto Vycor glass preheated at 773 K. The amount of adsorbed pyrene: —·—· 34 μg g^{-1}; ····· 1.1, —— 5.7 mg g^{-1}. The excitation wavenumber is 26950 cm^{-1} which corresponds to the ^1L_b region.

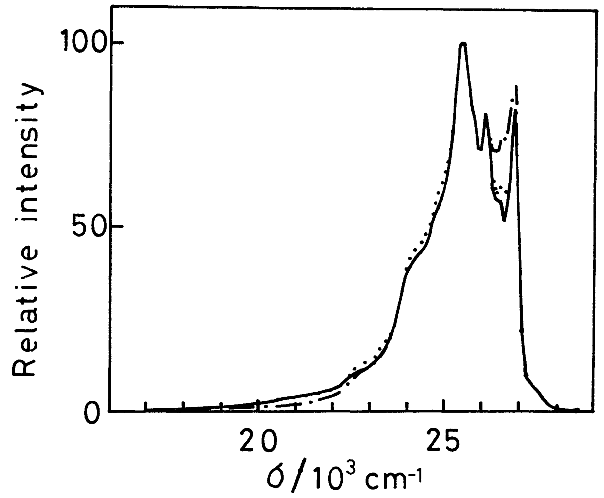

Fig. 2. The dependence of the fluorescence spectra of pyrene on the amount of pyrene adsorbed onto Vycor glass preheated at 773 K. The amount of adsorbed pyrene: —·—· 34 μg g^{-1}; ····· 1.1, —— 5.7 mg g^{-1}. The excitation wavenumber is 30030 cm^{-1} which corresponds to the ^1L_a region.

Figure 2 shows the fluorescence spectra of pyrene adsorbed on Vycor glass with the amounts of 34 μg g^{-1}, 1.1 mg g^{-1} and 5.7 mg g^{-1} at 295 K. The excitation wavenumber corresponds to the ^1L_a transition of pyrene. In contrast to the case excited with 26950 cm^{-1}, it is clearly seen there is no large difference among the fluorescence spectra upon the amount of adsorbed pyrene and that the entire fluorescence spectra consist of the monomer-like emission, exhibiting a sharp vibrational fine structure at around 24000—27000 cm^{-1}. The 26880 cm^{-1} band (the 0-0

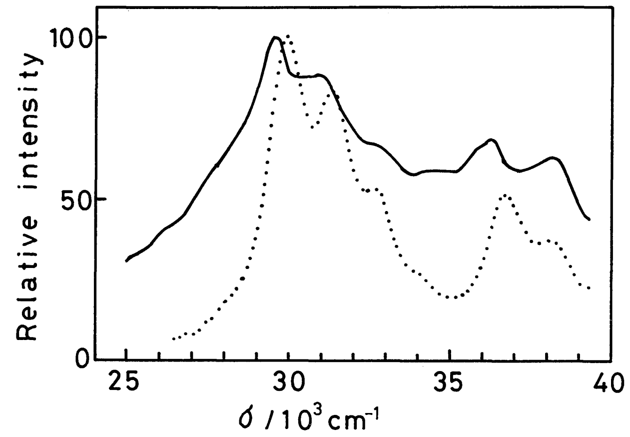

Fig. 3. The fluorescence-excitation spectra of pyrene adsorbed onto Vycor glass preheated at 773 K. The observed wavenumber: ····· 25450 cm^{-1} and —— 21280 cm^{-1} which correspond to the monomer-like and excimer-like emission, respectively. The amount of adsorbed pyrene is 34 µg g^{-1}.

band) has relatively high intensity as compared with that in solution. Such behavior was also observed for the fluorescence spectra of pyrene adsorbed on silica gel. These results indicate that the adsorbed pyrene molecules on the surfaces are surrounded by a more polar environment than in cyclohexana.[5–7,11–13,20] The monomer-like and excimer-like emissions in Figs. 1 and 2 are similar in their spectral shapes to those commonly observed in solution. This indicates little perturbation of these systems by the oxide support (a weak support effect).[34] In general, the influence of the adsorption on the ground and excited states of pyrene molecules onto the surface of Vycor glass is small.

It is noted that the intensity of the FE component excited at 29650 cm^{-1} is larger than that excited at 30300 cm^{-1}. Similar variation in the FE and FM emissions was observed for the fluorescence spectra of pyrene in the adsorbed state on silica gel surfaces.[20]

Figure 3 shows the fluorescence-excitation spectra of pyrene adsorbed on Vycor glass. The monitored wavenumbers of 25450 cm^{-1} and 21280 cm^{-1} correspond to the peak positions of the FM and FE fluorescence components, respectively. Even when pyrene is adsorbed on Vycor glass with the lowest surface coverage, i. e. 34 µg g^{-1}, the excitation spectra of the FM and FE fluorescence are not in accord with each other. These findings can be explained by the concept that the monomeric and dimeric pyrene species coexist on the surface of Vycor glass in the ground state. This coexistence of monomeric and dimeric pyrene species on the surface may be responsible for the excitation-wavenumber dependence of the fluorescence spectra of pyrene molecules adsorbed on Vycor glass shown in Figs. 1 and 2.

Time-Resolved Fluorescence Spectra. Figure 4 shows the time-resolved fluorescence spectra of pyrene adsorbed on Vycor glass with the amount of 0.11 mg g^{-1} at 295 K when the sample is excited at 29660 cm^{-1} corresponding to the ^1L_a region. Figure 4 also includes a steady-state fluorescence spectrum of pyrene in cyclohexane solution. All spectra are normalized to the maximum intensity. At first stage (spectrum a, 0—30 ns) the 0-0 band is located at 26600 cm^{-1} (376 nm, indicated by D). The intensity at around 21000 cm^{-1} is weak. There is a shoulder at around 26880 cm^{-1}. At the second stage (spectrum b, 30—70 ns), the contribution of 26600 cm^{-1} component is preferentially observed, although there is a peak at 26880 cm^{-1} (372 nm, indicated by M). This peak position is coincident with the 0-0 band of the steady-state fluorescence spectrum of monomeric pyrene in

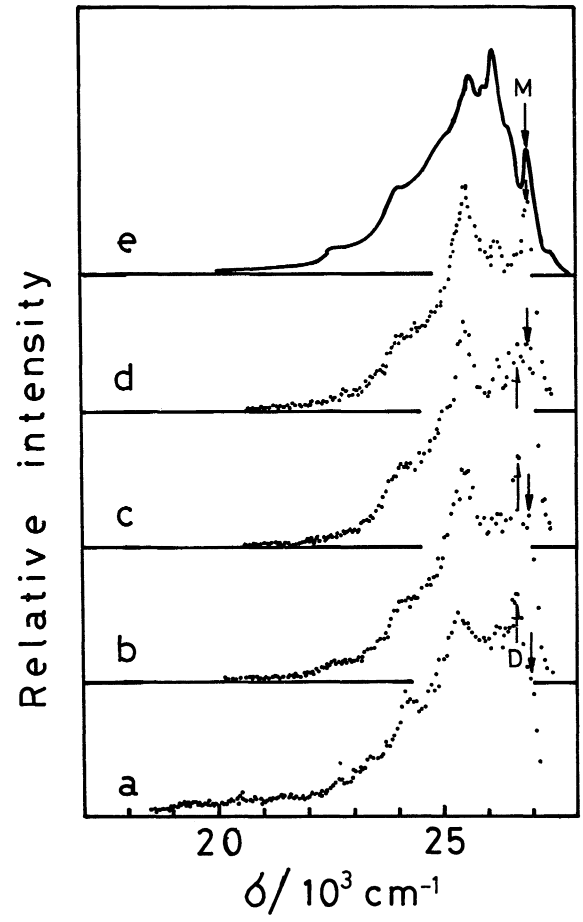

Fig. 4. The time-resolved fluorescence spectra of pyrene adsorbed onto Vycor glass (a—d), together with steady-state fluorescence spectrum(e) of cyclohexane solution. The amount of adsorbed pyrene is 0.11 mg g^{-1}. The excitation wavelength is 29660 cm^{-1}. The time zero corresponds to the time in which the intensity of excitation pulse reaches 5% of its maximum intensity. The time intervals for measuring the spectrum: (a) 0—30 ns, (b) 30—70 ns, (c) 110—180 ns, and (d) 270—450 ns. (e) 3.10×10^{-5} mol dm^{-3}. ↑ and ↓ represent the position of wavenumbers of 26600 cm^{-1} and 26880 cm^{-1}, respectively.

cyclohexane solution (spectrum e). At the third stage (spectrum c, 110—180 ns), the component indicated by D has nearly the same intensity as one indicated by M. At the forth stage (spectrum d) the intensity of the spectrum around 21000 cm^{-1} becomes very weak as compared with those of the spectra a and b. The intensity of the band at around 26880 cm^{-1} becomes very strong and sharp, and the component, the peak of which is at 26600 cm^{-1}, becomes very weak. It is seen from the spectrum of e, which was observed in cyclohexane solution, that the spectrum has a peak at 26880 cm^{-1} (the 0-0 band).[22]

As shown in Fig. 4, at the first stage the 0-0 band peak is observed at 26600 cm^{-1} (376 nm). This peak is shifted by 280 cm^{-1} (4 nm) to the red compared with the 0-0 band M (26880 cm^{-1}) that appears in a longer time region. This amount of red shift is in fair agreement with the results reported in the LB-film.[17,18] Therefore the band appearing at 26600 cm^{-1} (376 nm) can safely be assigned to the 0-0 band of dimeric pyrene adsorbed onto Vycor glass.

The changes in the fluorescence spectra with time indicate that there are at least three different fluorescent species on the surfaces and the extent of their contribution to the entire fluorescence changes with time. In other words, the concentrations of the species contributing to the emissions at around 26600 and 21000 cm^{-1} decrease and simultaneously the contribution to the emission at 26880 cm^{-1} increases. It should be pointed out that the adsorbed dimeric pyrene molecules have the geometries favorable to form an excimer conformation soon after excitation on the surface of Vycor glass. The possibility of excitation energy transfer[18,35,36] between pyrene molecules adsorbed on the surface ought to be negligibly small because the 26600 cm^{-1} peak was observed even under conditions of very small surface coverage (0.0014).[25] The small overlap between absorption and fluorescence spectra of pyrene ought to be also responsible for the negligibly small energy transfer between pyrene molecules adsorbed on Vycor glass.

Decay of Excited Pyrenes Adsorbed on Porous Vycor Glass. The decay curves of the fluorescence of adsorbed pyrene molecules on Vycor glass shown in Fig. 5 are found to be nonexponential. The deconvolution was carried out by the usual three exponentials.[14,37—39] The obtained values of individual lifetimes are given in Table 1. It was found that they qualitatively correspond to those adsorbed on modified silica gel surfaces obtained by Avnir et al. (ca. 36—45, 186—230, and 389—392).[14] From the comparison with the literature data of lifetimes and in referring to the preexponential factors, one can assign $t1$ component to the monomer emission and $t3$ to the excimer emission. In this case the excimer is formed in

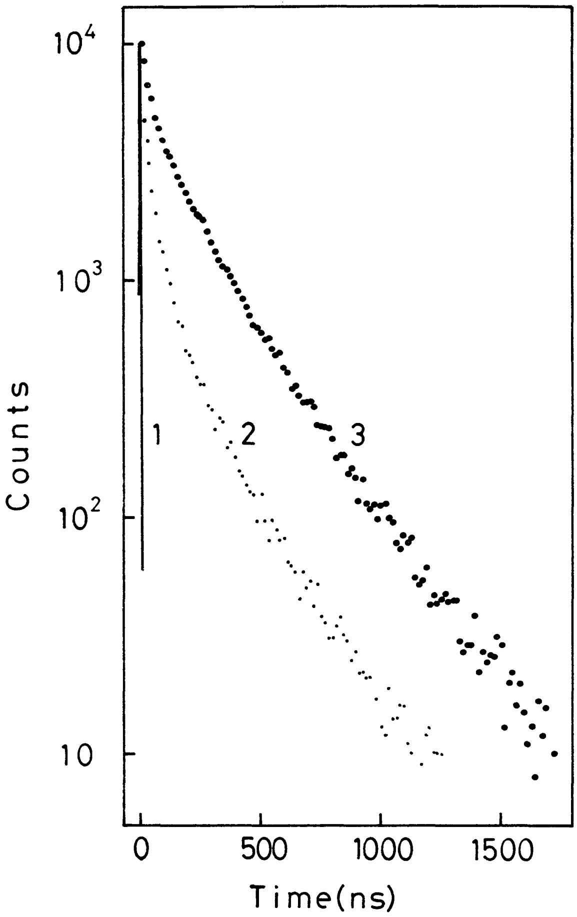

Fig. 5. Decay curves of the fluorescence of pyrene adsorbed onto Vycor glass. The amount of adsorbed pyrene is 34 μg g^{-1}. Observed wavenumber: (2) 21280 cm^{-1}; (3) 25450 cm^{-1}. The wavenumber of the excitation pulse (1) is 29660 cm^{-1}. The decay curves were fitted by $I=\exp(-t/t1)+c2\exp(-t/t2)+c3\exp(-t/t3)$.

Table 1. Lifetimes of the Emission of Pyrene Adsorbed on Porous Vycor Glass. $C2$ and $C3$ are the Preexponential Factors Corresponding to the $t2$ and $t3$ Components, Respectively, Where the Preexponential Factor of $t1$ Component is Fixed to 1.0

Amount of adsorbed pyrene	em.	$t1$	$t2$	$t3$	$c2$	$c3$
mg g^{-1}	cm^{-1}		ns			
0.034	25450	309	134	24	1.5	2.3
	21280	303	100	19	4.8	33
6.0	25450	355	145	20	0.85	0.76
	21280	344	126	48	7.0	34

a process involving no substantial diffusion on the the surface of Vycor glass.

As shown above, the spectrum of Fig. 4a suggests that there is a fluorescence component around 25000 cm^{-1} (compare Fig. 4d with Fig. 4a) and the peak shift from 26600 cm^{-1} to 26880 cm^{-1} coincides with that from dimeric to monomeric pyrene observed in the LB film. *T*2 component can, therefore, be assigned to the emission of dimeric spsecies, which may be formed from the weakly bound ground-state pyrene molecules on the surface of Vycor glass.

In Table 1, the lifetime of 100—145 ns is much longer than that of the corresponding dimer species observed in the LB film. Such difference seems to reflect the difference in properties of the environment surrounding pyrene molecules, the mobility of pyrene molecules, the fractal dimension(which is estimated to be 2.8 for Vycor glass and 2.0 for LB film)[40] between Vycor glass and LB film, etc.

It is well-known that the S_0–S_1 transition of pyrene molecule is symmetry forbidden. The radiative and intersystem-crossing rate constants of pyrene in cyclohexane, k_{FM} and k_{TM}, are estimated to be 1.5×10^7 and 7.8×10^6 s^{-1}, respectively.[22] These values are much smaller than the values of molecules where S_0–S_1 transition is symmetry allowed. The rate constants of pyrene molecule are, therefore, much more dependent on the circumstances. Table 1 shows that the lifetimes of individual components with lower surface coverage have shorter values than those with higher surface coverage. The results indicate that the circumstance of adsorbed pyrene on porous Vycor glass with lower surface coverage somewhat differs from that with higher surface coverage. This difference corresponds to properties of various types of the surface hydroxyl groups of porous glasses.[28–31]

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26) Through the present work, the evacuated temperature, 373 K, was used to remove remaining cyclohexane. When the sample were evacuated at the temperature of 338 K, growing-in of the excimer emission at 21280 cm^{-1} was observed. This result indicated that excimer formation due to diffusion on the surface occurred, showing the remaining cyclohexane in Vycor glass support. On the other hand, when the samples were evacuated at 373 K, no growing-in of the excimer emission at 21280 cm^{-1} was observed within the time-resolution (0.5 ns) of the experiments. This observation indicated that excimer-like emission observed in this experiments is originated from ground-state aggregates.

27) The molecular dimensions of the pyrene molecule are 7.2 Å by 13.0 Å.[16] Based on the values, a surface area adsorbed by a pyrene molecule is estimated to be 93.6 Å^2. This value is 62.4% compared with our adopted value, 150 Å^2.[10,11,20]

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