Supporting Information

Excimer Luminescence From Nonresonantly Excited Pyrene and Perylene Molecules in Solution

Kazuya Nakagawa[1], Yudai Numata[1], Heisuke Ishino[1], Daichi Tanaka[1], Takayoshi Kobayashi[2], and Eiji Tokunaga[1,3*]

[1]Department of Physics, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan
[2]Advanced Ultrafast Laser Research Center, University of Electro-Communications, 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585 Japan
[3]Research Center for Green and Safety Sciences, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

[*]Corresponding author; email address: eiji@rs.kagu.tus.ac.jp

The Effect of Dissolved Oxygen in Solution

It is known that dissolved oxygen quenches photoluminescence of molecules in solution [3], but we did not deoxygenate the solution samples for stable measurement: For perylene in toluene, we confirmed that there is little difference in the photoluminescence spectra between samples thus prepared and those bubbled with nitrogen gas for dissolved oxygen to be expelled. For pyrene in ethanol, on the other hand, the photoluminescence intensity in the solution exposed to air, where dissolved oxygen was equilibrated with ambient air, was reduced by about 35% compared with that in the solution bubbled with nitrogen as shown in Fig. S1. We found that even if the bubbled solution was sealed in a cuvett with a screw cap, the PL intensity was gradually reduced to almost the same level within two hours as that saturated with air. Therefore, we intentionally did not degas the solution but used it as saturated with ambient air for stable measurement.

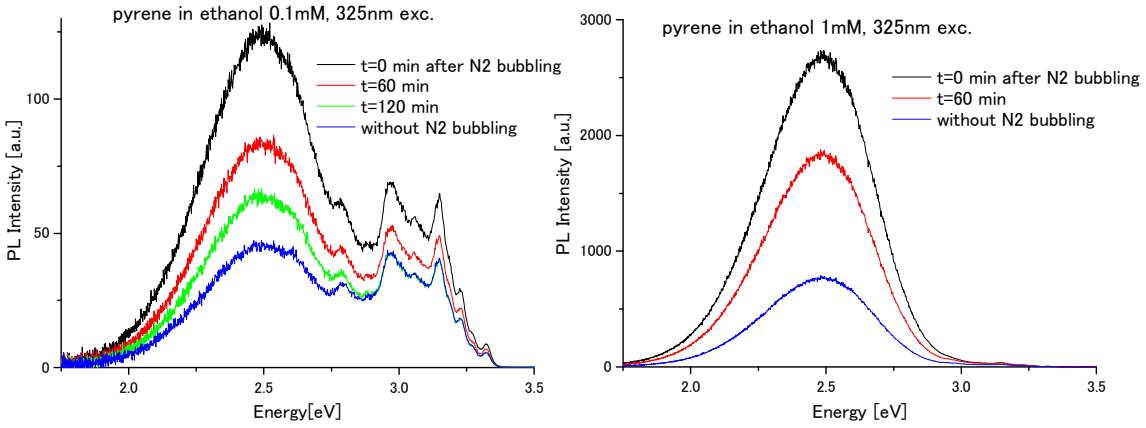

Fig. S1: The effect of nitrogen gas bubbling on the photoluminescence intensity for pyrene in ethanol by resonant excitation at 325 nm. Left: 0.1 mM solution, Right: 1 mM solution.

We performed a time-resolved photoluminescence measurement on the excited-state lifetime of pyrene monomers in air-saturated ethanol solution for providing the experimentally determined parameter in the fitting in Fig.7. A 0.03 mM dilute solution of pyrene in ethanol was excited by 600 ps UV laser pulses at 337.1 nm from a nitrogen laser (Usho, KEN-910T). The photoluminescence spectra from pyrene monomers were time-resolved with an intensified CCD camera (Andor) through a polychromator (Andor, MS200) with 5 ns time resolution determined by the gate width. Fig. S2 shows the time-resolved, spectrally integrated luminescence from pyrene monomers exhibiting 19.9 ns decaytime, which is much shorter than 290 ns in deoxygenated solution [4]. This large reduction in the decaytime agrees with the previous report [3]. As the given parameter for the lifetime of pyrene monomers, τ_m =19.9 ns was used for the fitting in Figs. 7.

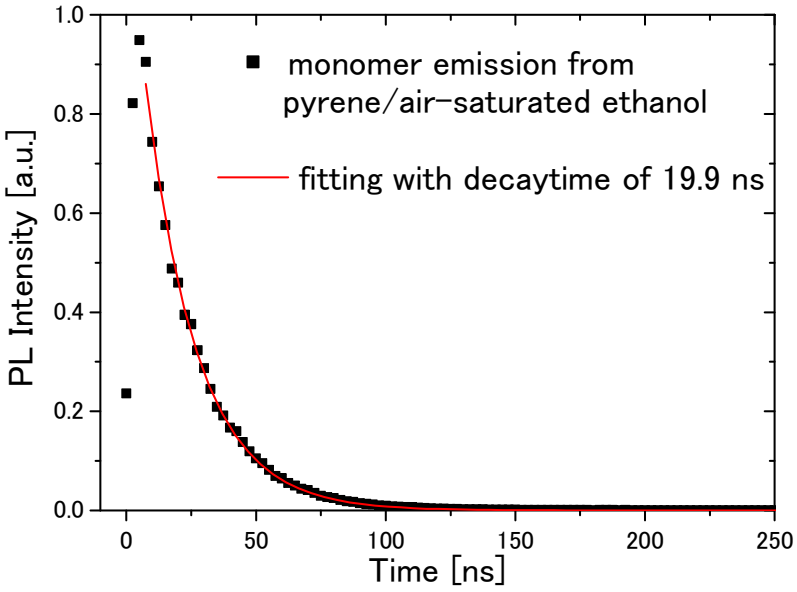

Fig. S2: Time resolved luminescence from pyrene monomers excited at 337.1 nm with 5 ns time resolution. The whole emission spectra were spectrally integrated exhibiting 19.9 ± 0.14 ns decaytime.

In preparing perylene in PMMA film, too, chloroform solution was not deoxygenated.

The Possibility of Crystal Formation in Perylene/PMMA Film

The effect of nonresonant excitation of perylene in PMMA was studied in Fig. 5. If monomer molcules are not homogeneously dispersed but locally aggregated in the polymer films, microcrystals should be formed to cause excimer emission of crystal origin. In order to claim that excimer emission is due to monomers which are accidentally located closely in polymer, one needs to find evidence that microcrystals are not formed anywhere over the films. We checked this by measuring space-resolved extinction spectra of the films.

Fig. S3(a) shows the photographs of the film at 1.5 and 5.0 mol%. Fig. S3(b) shows macroscopic extinction spectra of 1.0 and 5.0 mol% films. Crystal formation in the 5.0 mol% film is evidenced by crystal spectra in Fig. S3(b), and no crystal formation in the 1.0 mol% film is evidenced by no crystal features in the spectrum in Fig. S3(b). One can not, however, reject the possibility of existence of minute crystals below the detection limit of the extinction spectral measurement.

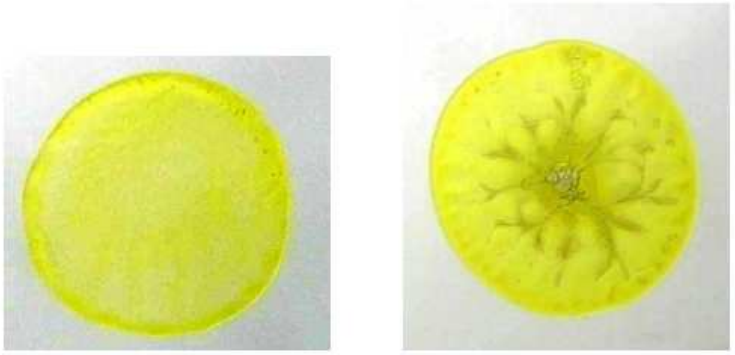

Fig. S3(a): PMMA films doped with perylene. Left:1.5mol% Right:5.0mol%

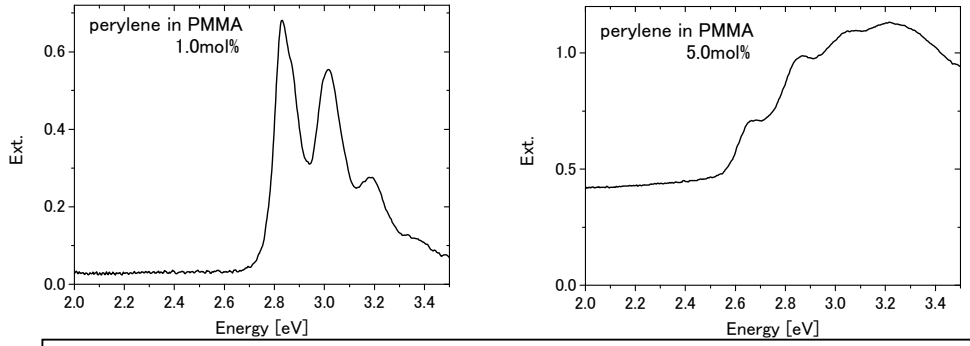

Fig. S3(b): Macroscopic extinction spectra of the 1.0 mol% and 5.0 mol% films.

Therefore, we checked whether microcrystals were formed in the films by measuring the extinction spectral images of the films as follows. White light from a Xe lamp was focused through 400 μm pinhole and the pinhole image was magnified by 6 times at a sample film to obtain the transmitted light image of ϕ2.4 mm just behind the sample. This image was transferred by 1/2 times magnification on the 16×16 fiber array of 0.96×0.96 mm^2 dimension. The 16×16 two-dimensional image was then rearranged to the 1×256

one-dimensional image to fit the entrance slit of a monochromator. Both spatially and spectrally resolved image of the sample was detected with a cooled CCD camera. As a result, we confirmed that there is no crystal formation observed over the whole film area with 0.12 mm resolution at 0.1, 0.5, 1.0, and 1.5 mol% concentration while microcrystals are formed at 3.0 and 5.0 mol%.

Figs. S4(a),(b),(c), and (d) are the photograph, the macroscopic extinction spectrum over the area of 4×1.5 mm^2, the extinction spectral images Ext(x, y, $\lambda = 465$ nm) and Ext(x, $y = 0.64$ mm, λ) of the film at 1.5 mol%, respectively. Both macroscopic and microscopic extinction spectra show monomer absorption spectra. The film is almost homogeneous and there is no feature of crystal spectra for any spot of 0.12×0.12 mm^2 area over the film. Similarly, we confirmed that there is no crystal formation for the films at 0.1, 0.5, and 1.0 mol%. Because the film was made by casting, the film is not uniformly made in thickness. Therefore light scattering is enhanced at some spots as in Fig. S4(c), but there is no crystal peak found in the space-resolved spectra as in Fig. S4(d).

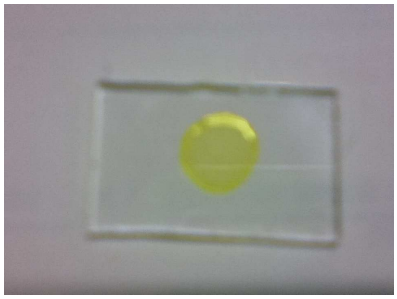

Fig. S4(a):Photo of 1.5 mol% perylene/PMMA film.

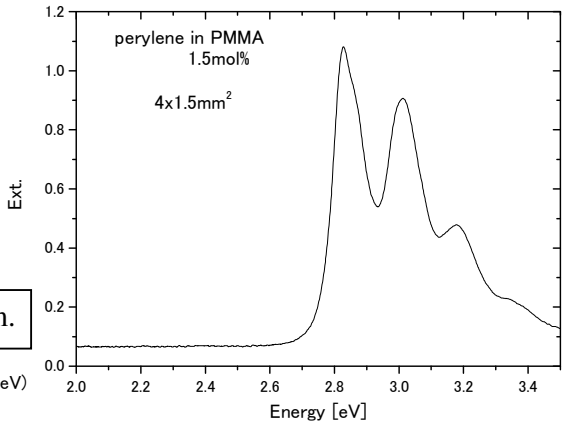

Fig. S4(b): Macroscopic extinction spectrum over the area of 4×1.5 mm^2 on the 1.5 mol% film.

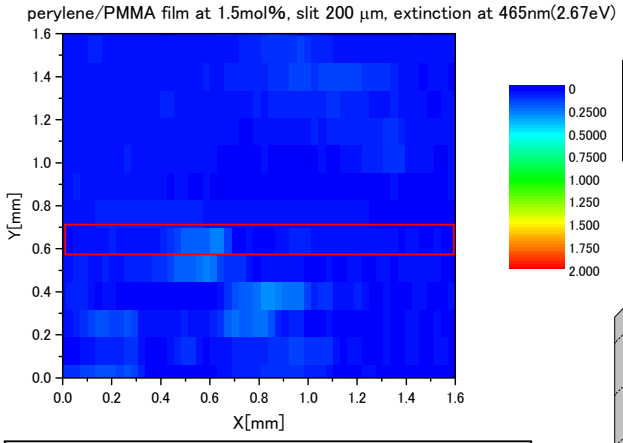

Fig.S4(c): Space-resolved extinction image at 2.67eV; Ext(x, y, $\lambda = 465$ nm).

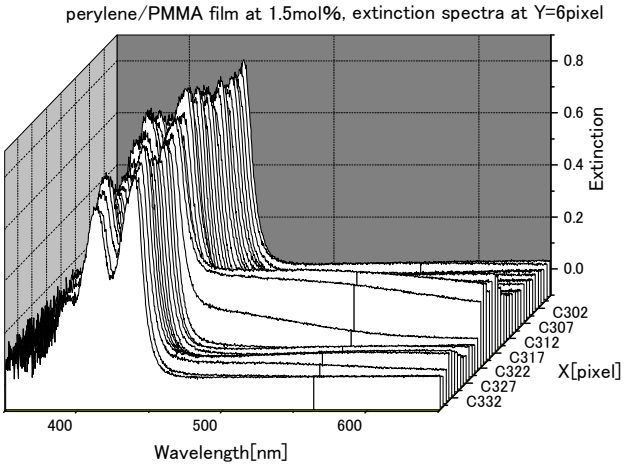

Fig.S4(d):Extinction spectra at $y = 0.64$ mm; Ext(x, $y = 0.64$ mm, λ).

Figs. S5(a),(b),(c), and (d) are the photograph, the macroscopic extinction spectrum over the area of 4×1.5 mm^2, the extinction spectral images Ext(x, y, $\lambda = 465$ nm) and Ext(x, $y = 1.1$ mm, λ) of the film at 3.0 mol%, respectively. Both macroscopic and microscopic extinction spectra show crystal formation in the film as indicated by a structure around 2.67 eV, which shows the free exciton peak. The exciton structure is seen to be inhomogeneously distributed over the film from Ext(x, y, λ) spectra in Figs. S5(c) and (d).

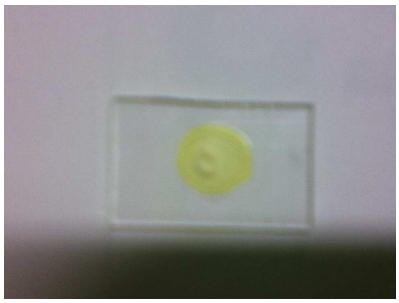

Fig. S5(a):Photo of 3.0 mol% perylene/PMMA film.

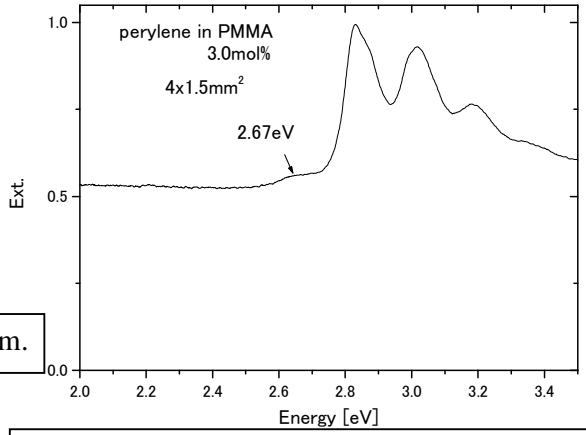

Fig. S5(b): Macroscopic extinction spectrum over the area of 4×1.5 mm^2 on the 3.0 mol% film.

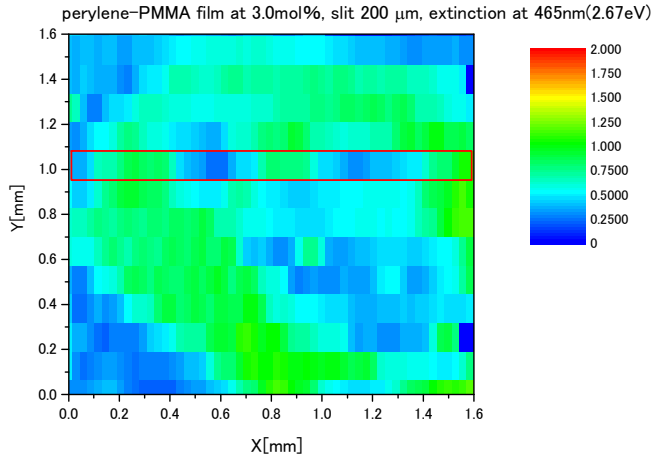

Fig. S5(c): Space-resolved extinction image at 2.67eV; Ext(x, y, $\lambda = 465$ nm).

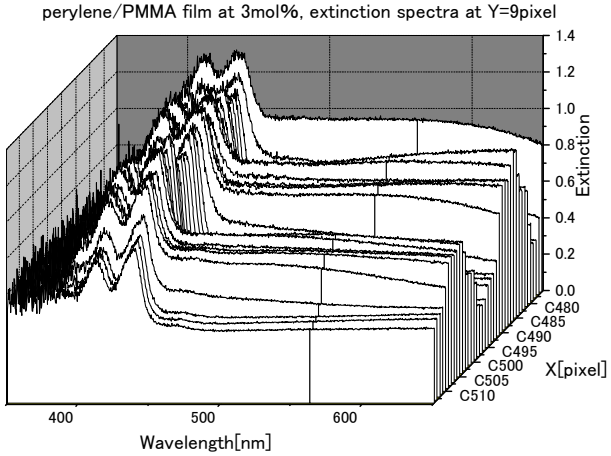

Fig. S5(d):Extinction spectra at $y = 1.1$ mm; Ext(x, $y = 1.1$ mm, λ).

The Concentration Dependence of Luminescence and Absorption Spectra in Solution

For solution samples, there was no significant concentration dependence both in emission and absorption spectral shapes as follows.

We compared the spectral shape of excimer emission as a function of concentration. There should be a recognaizable, systematic change in the spectral shape depending on the concentration if aggregates contribute to the excimer emission because the size and the number of aggregates should depend sensitively on the concentration. As shown in Figs. S6, there is no appreciable dependence of the spectral shape on the concentration. We believe this fact suggest that the contribution of aggregates is marginal.

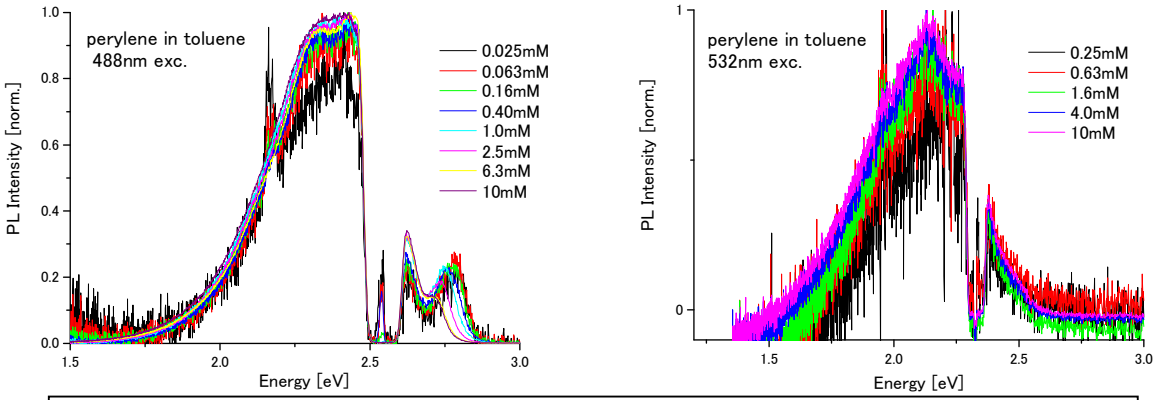

Fig. S6(a): Photoluminescence spectra by nonresonant excitation of perylene in toluene

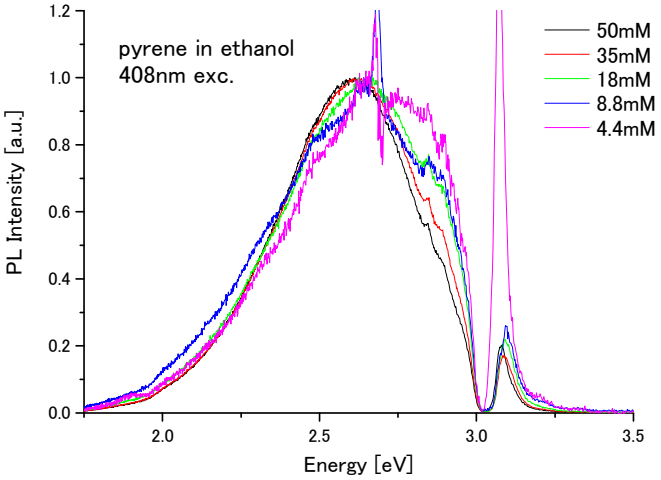

Fig. S6(b): Photoluminescence spectra by nonresonant excitation of pyrene in ethanol

As shown in Figs. S7, we also checked the concentration dependence of absorption spectra below the absorption edge of pyrene in ethanol and perylene in toluene . (The whole absorption spectra are difficult to detect even at 1 mM because of saturation.) We detect no appreciable signature of aggregates for both pyrene and perylene below the absorption edge. For both pyrene and perylene, as the concentration is increased, there is a relative increase in the absorption for higher energy region. This is consistent with the report by J. Ferguson [24], probably indicating dimer (excimer) formation. This (the presence of molecule pairs with dimer configuration) is within our model as depicted in Fig.10.

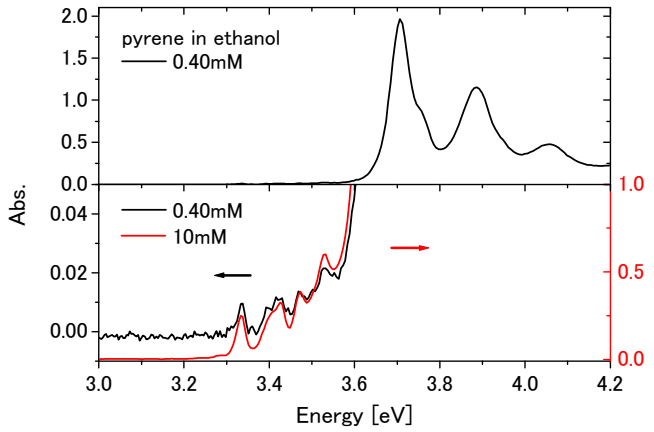

Fig. S7(a): Absoption spectra of pyrene in ethanol.

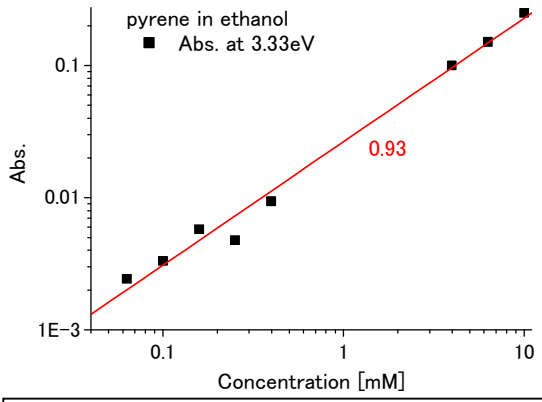

Fig. S7(b): Concentration dependence of absorbance at 3.33 eV of pyrene in ethanol.

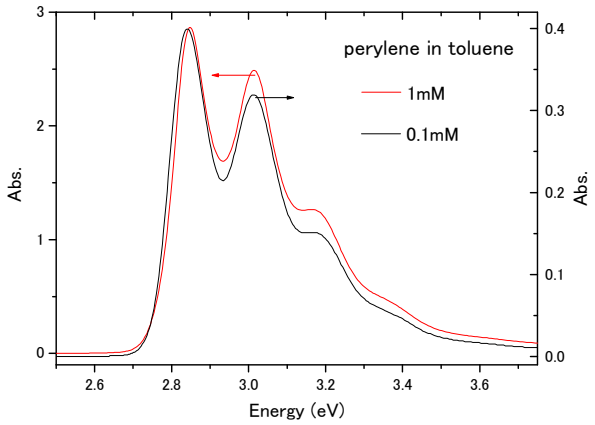

Fig. S7(c): Absoption spectra of pyrene in ethanol at various concentrations.

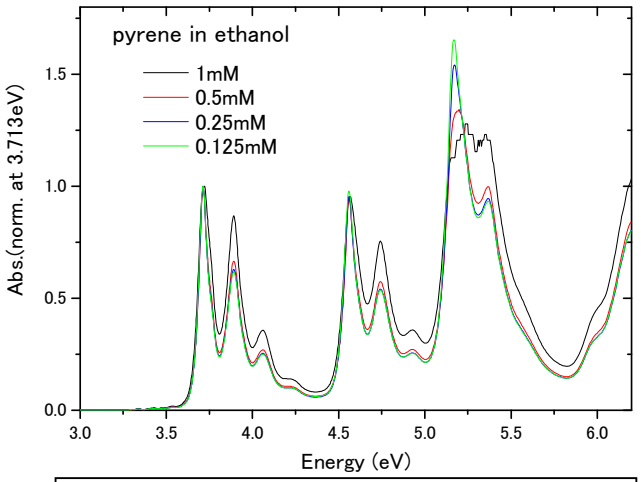

Fig. S7(d):Normalized absoption spectra of perylene in toluene at various concentrations.