Fluorescent Nanoparticles of 2-Ethylanthracene and Pyrene

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Fluorescence behavior of nanoparticles of two aromatic compounds, 2-ethylanthracene and pyrene, was studied. Doped nanoparticles were also studied. Transparent organic nanoparticles dispersed in water were prepared by reprecipitation method. Polyvinyl alcohol was added in water to improve stability of organic nanoparticles. Fluorescence spectra and fluorescence quantum yields were measured by an absolute photoluminescence quantum yield measurement system. Fluorescence lifetimes were measured with a combination of a femtosecond Ti:sapphire laser and a streak camera. Fluorescence behavior of 2-ethylanthracene nanoparticles doped with naphthacene, pyrene nanoparticles doped with perylene, and polycrystals of 2-ethylanthracene and pyrene, was measured. Doping of nanoparticles with dopant quenched fluorescence of nanoparticles and strong fluorescence of dopant was observed. Fluorescence quantum yield of 2-ethylnaphthacene nanoparticles doped with naphthacene and that of pyrene nanoparticles doped with perylene were as high as 0.52 and 0.58, respectively.
Key words: Nanoparticle, Florescence quantum yield, Fluorescence spectrum, 2-Ethylanthracene, Pyrene

1. INTRODUCTION

Nanoparticles are very attractive materials. Nanoparticles of metals and semi-conductors have properties different from crystals or atoms. Energy of electrons in a metal or semiconductor nanoparticle depends on the particle size significantly due to quantum effects. On the other hand, properties of organic nanoparticles have not been fully clarified yet.

Nanoparticles of organic compounds are expected to be durable against strong laser light because of their short lifetimes of excited states. In these twenty years, fine particles of organic compounds were prepared by reprecipitation method, and their optical properties have been studied [1-4].

We have already reported two-photon absorption cross sections of nanoparticles of naphthalocyanine derivatives [5], third-order nonlinear optical properties of several organic nanoparticles [6], and fluorescence behavior of organic nanoparticles, mainly of anthracene nanoparticles [7]. In this study, we measured UV/visible absorption spectra, fluorescence spectra, fluorescence quantum yields, and fluorescence lifetimes, of organic nanoparticles. Fluorescence quantum yield of 2-ethylnaphthacene nanoparticles doped with naphthacene and that of pyrene nanoparticles doped with perylene were as high as 0.52 and 0.58, respectively.

2. EXPERIMENTAL

Figure 1 shows structural formulas of organic compounds studied. Those compounds were purified by several time recrystalization. Transparent organic nanoparticles dispersed in water were prepared by reprecipitation method. [1-4] Typical condition for preparing nanoparticles was as follows: 1 ml of acetone solution of 2-ethylanthracence (ca. 2×10^{-3} M) was injected using a syringe into 100 ml of water stirred vigorously at ca. 10°C. A dopant (naphthacene) was added in acetone solutions at a very low concentration. PVA (100 ppm) was added to the water to stabilize nanoparticles in water.
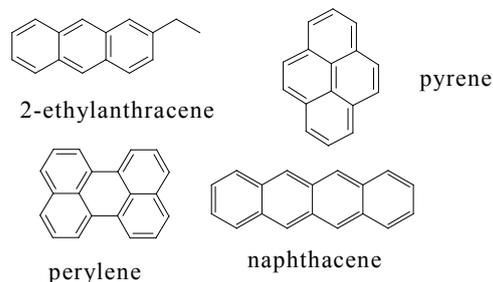
Fig. 1. Structural formulas of organic compounds studied.

Fluorescence spectra and fluorescence quantum yields were measured by an absolute PL quantum yield measurement system (Hamamatsu Photonics, C9920-03G). Fluorescence lifetimes were measured with a combination of a femtosecond Ti:sapphire laser and a streak camera. In order to analyze the fluorescence decay curves, they were simulated. The observed fluorescence decay curve, I(t), is assumed to be expressed by the following convolution integral

$$I(t) = \int_0^t L(t')R(t-t')dt' \qquad (1)$$

where L(t) is the temporal profile of the laser pulse, and R(t) is the response of the sample irradiated by a laser with an ideal delta function shape pulse. R(t) is assumed to be a single exponential function. Sometimes R(t) is assumed a double exponential function

$$R(t) = a_1\exp(-t/t_1) + a_2\exp(-t/t_2) \qquad (2)$$

All the parameters in equation 2 and the time difference between the experimental and simulated fluorescence decay curves, Δt, were determined using a nonlinear, least-squares iterative convolution method based on the Marquardt algorithm [8,9]. Scattered light of a laser pulse is used as L(t).

3. RESULTS AND DISCUSSION

Figures 2 and 3 show the UV/visible absorption spectra of 2-ethylanthracene nanoparticles and those of pyrene nanoparticles. Very little amount of dopant gave no influence on the absorption spectra of both matrixes. Doping anthrancene nanoparticles with naphthacence does not change UV/visible absorption spectra because of very low concentration of the dopant.

Figure 4 shows fluorescence spectra of 2-ethylanthracene nanoparticles doped with naphthacence. Exciting wavelength was 375 nm. The fluorescence spectrum of 2-ethylanthracene nanoparticles without dopant shows fluorescence longer than ca. 430 nm with a weak vibronic structure. Doping of naphthacene decreased fluorescence of 2-ethylanthracene nanoparticles and strong fluorescence of naphthacene appeared. Fluorescence of 2-ethylanthracene nanoparticles almost disappeared at a doping concentration of as low as 0.5 mol%. For anthracene nanoparticles doped with naphthacence, fluorescence of anthracene nanoparticles almost disappeared at a doping concentration of 0.05 mol%. Since doping concentration was estimation based on calculation, it must be more difficult to dope naphthacene into 2-ethylanthracene nanoparticles than into anthracene nanoparticles. We could not dope enough amount of perylene into 2-ethylanthracene nanoparticles.

Figure 5 shows fluorescence spectra of pyrene nanoparticles doped with perylene. Exciting wavelength was 375 nm. The fluorescence spectrum of pyrene nanoparticles without dopant shows weak broad fluorescence band around 450 nm without any vibronic structures. This spectrum is very similar to that of pyrene polycrystals (see Fig. 6). Doping of perylene decreased fluorescence of pyrene nanoparticles and strong fluorescence of perylene appeared. Fluorescence of pyrene nanoparticles almost disappeared at a doping concentration of 0.1 mol%. We could not dope enough amount of naphthacene into pyrene nanoparticles.
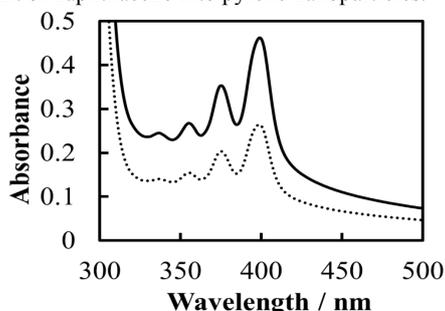
Fig. 2. Ultraviolet/visible absorption spectra of 2-ethylanthracene nanoparticles (solid line) and that of 2-ethylanthracene nanoparticles doped with naphthacene (dotted line).
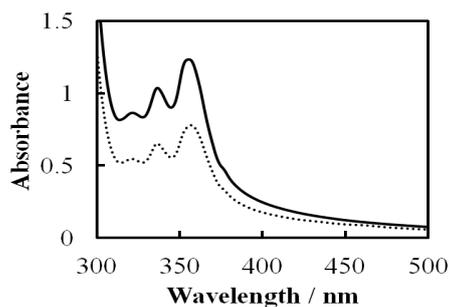
Fig. 3. Ultraviolet/visible absorption spectra of pyrene nanoparticles (solid line) and that of pyrene nanoparticles doped with perylene (dotted line).
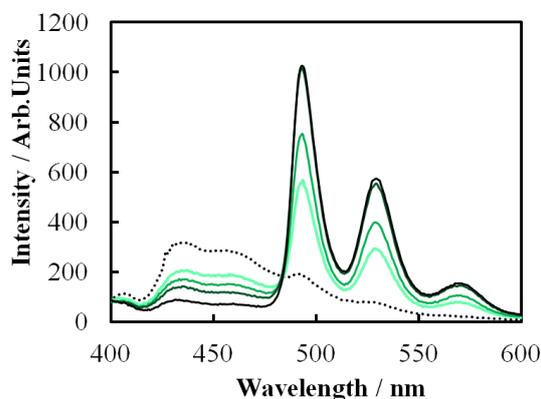
Fig. 4. Fluorescence spectra of 2-ethyl-anthracene nanoparticles and 2-ethyl-anthracene nanoparticles doped with naphthacene. The dope concentration of naphthacene: 0 mol% (black dotted line), 0.05 mol% (the lightest green line), 0.1 mol% (green line), 0.25 mol% (the darkest green line), 0. 5 mol% (black solid line).
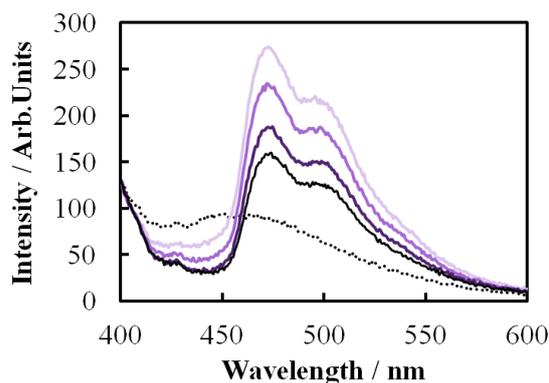
Fig. 5. Fluorescence spectra of pyrene nanoparticles doped with perylene. The dope concentration of perylene: 0 mol% (black dot line), 0.05 mol% (the lightest purple dotted line), 0.1 mol% (purple line), 0.5 mol% (the darkest purple line), 0.75 mol% (black solid line).

Figures 7 and 8 show the dependences of fluorescence quantum yield on doping concentration for 2-ethylanthracene nanoparticles doped with naphthacence and pyrene nanoparticles doped with perylene, respectively. The largest value of fluorescence quantum yield of naphthacene doped 2-ethylanthracence nanoparticles was as high as 0.52 at a naphthacene concentration of 1.0 mol%. The largest value of fluorescence quantum yield of perylene doped pyrene nanoparticles was as high as 0.58 at a perylene concentration of 0.1 mol%. Quenching was observed for both cases at high doping concentrations. Table I summarized fluorescence quantum yields of nanoparticles and polycrystals of organic compounds studied.

Table I   Fluorescence quantum yields of nanoparticles and polycrystals of organic compounds studied.

Sample		Fluorescence quantum yields
perylene	polycrystals	0.38
	nanoparticles	0.20
2-ethylanthracene	polycrystals	0.10
	nanoparticles	0.23
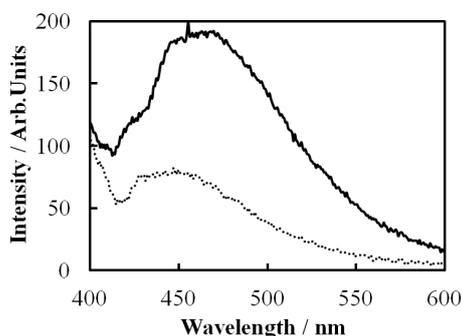
Fig. 6. Fluorescence spectra of pyrene polycrystals (solid line) and 2-ethyl-anthracene polycrystals (dotted line).
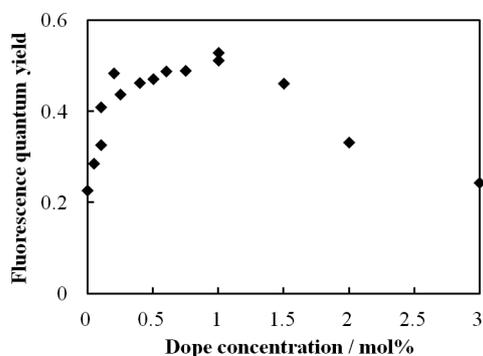
Fig. 7. The dependence of fluorescence quantum yield of naphthacene doped 2-ethylanthracene nanopariticles on dopant concentration.
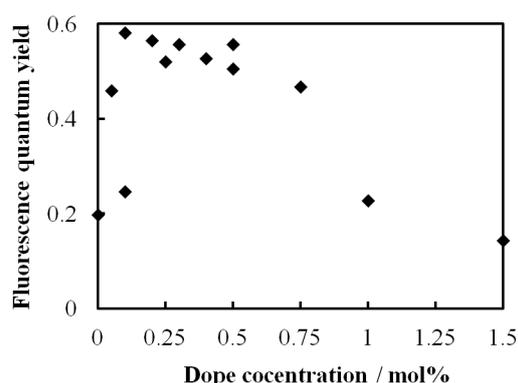
Fig. 8. The dependence of fluorescence quantum yield of perylene doped pyrene nanopariticles on dopant concentration .
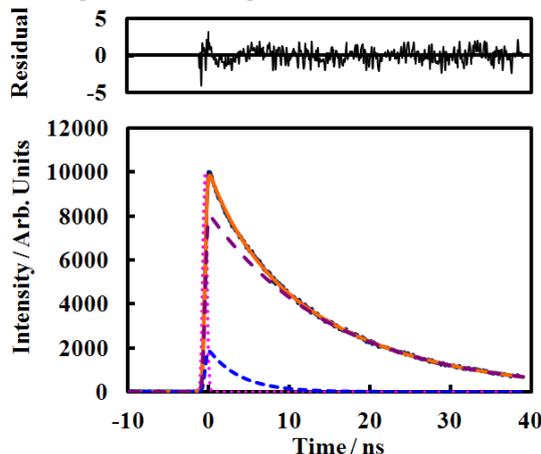
Fig. 9. Fluorescence decay curve of naphthacene doped 2-ethylanthracene nanoparticles and its simulation. The dope concentration of naphthacene: 0.5mol%. Fluorescence intensity (dark blue solid line), laser (pink dotted line), simulation (orange solid line), first exponential (blue dotted line), second exponential (dark red broken line).
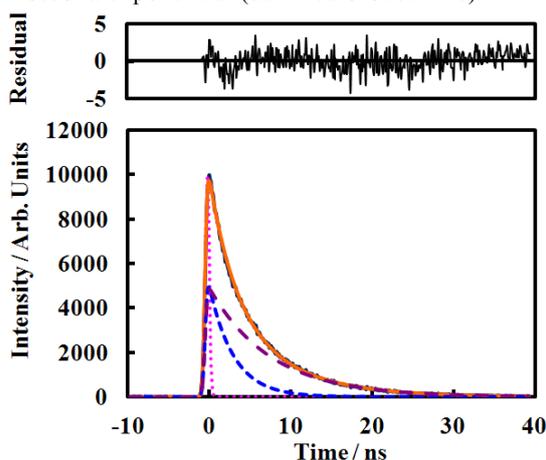
Fig. 10. Fluorescence decay curve of peylene doped pyrene nanoparticles and its simulation. The dope concentration of perylene: 0.5mol%. Fluorescence intensity (dark blue solid line), laser (pink dotted line), simulation (orange solid line), first exponential (blue dotted line), second exponential (dark red broken line).

Table I summarized fluorescence quantum yields of nanoparticles and polycrystals of organic compounds studied. The value of fluorescence quantum yield of 2-ethylanthracene nanoparticles was almost same as that of porycrystals. This value was better than that of anthracene nanoparticles (ca. 0.10). Although pyrene polycrystals have relatively high fluorescence quantum yield, nanoparticles of pyrene had lower fluorescence quantum yield. We think that the difference of fluorescence quantum yield between polycrystals and nanoparticles comes from amorphous character of nanoparticles.

Fluorescence decay curve of naphthacene doped 2-ethylanthracene nanoparticles was not single exponential (see Figs. 9 and 10). We assumed double exponential response for fluorescence of nanoparticles. The results of lifetime measurements are summarized in Table II. Dopant concentration affected very slightly to fluorescence lifetimes until a doping concentration of 1 mol%.

The results of lifetime measurements for perylene doped pyrene nanoparticles are summarized in Table III. We could not measure fluorescence decay curves of pyrene nanoparticles because of their short absorption wavelength. Higher doping concentration gave shorter fluorescence lifetimes of dopant, perylene. This is probably due to dimer formation of dopant in a nanoparticle.

Polycrystals of 2-ethylanthracene and pyrene show shorter fluorescence lifetimes than nanoparticles (see Tables II and IV). The reason is not clear at the moment.

Figure 11 shows a photograph of naphthacene doped 2-ethylanthracence nanopariticles excited by 400 nm laser radiation. Strong green emission was observed.

Table II. Fluorescence lifetimes of naphthacene doped 2-ethylanthracene nanoparticles

concentration of naphthacene / mol%	Fluorescence lifetime / ns	
	Fast(Weight)	Slow(Weight)
0	1.51 (86.3%)	9.46 (13.7%)
0.25	3.75 (11.2%)	16.7 (88.8%)
0.50	3.92 (20.5%)	15.7 (79.5%)
1.00	6.28 (12.5%)	15.6 (87.5%)

Table III. Fluorescence lifetimes of perylene doped pyrene nanoparticles

concentration of perylene / mol%	Fluorescence lifetime / ns	
	Fast(Weight)	Slow(Weight)
0	- (-)	- (-)
0.25	4.21 (52.1%)	9.39 (47.9%)
0.50	3.00 (53.0%)	7.51 (47.0%)
1.00	2.70 (60.4%)	6.84 (39.6%)

Table IV. Fluorescence lifetimes of polycrystals of organic compounds studied.

sample	Fluorescence lifetime / ns	
	Fast(Weight)	Slow(Weight)
2-ethyl-anthracece	0.70 (91.1%)	6.67(8.9%)
pyrene	2.76 (33.1%)	22.1 (66.9%)
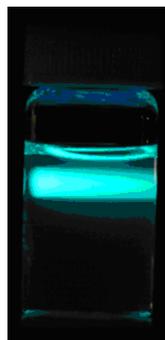
Fig. 11. Photograph of naphthacence doped 2-ethylanthracence nanopariticles excited by 400 nm laser radiation.

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