FLUORESCENT NANOPARTICLES OF ANTHRACENE AND BIS-MSB

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ABSTRACT

Fluorescence behavior of nanoparticles of two compounds, anthracene and 1,4-bis(2-methylstyryl)benzene (bis-MSB), was studied. Doped nanoparticles were also studied. Transparent organic nanoparticles dispersed in water were prepared by reprecipitation method. Poly(vinyl alcohol) was added into 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 anthracene nanoparticles doped with perylene, anthracene nanoparticles doped with naphthacene, bis-MSB nanoparticles doped with perylene, and bis-MSB nanoparticles doped with naphthacene, was measured. When doping nanoparticles with a dopant, fluorescence of nanoparticles was quenched and strong fluorescence of dopant was observed. Fluorescence quantum yields of both anthracene nanoparticles doped with naphthacene and anthracene nanoparticles doped with perylene were as high as 0.75.
KEYWORDS: Nanoparticle, Florescence quantum yield, Fluorescence spectrum, Anthracene, Bis-MSB

1. INTRODUCTION

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

Nanoparticles of organic compounds are expected to be durable against strong laser light because of their short lifetimes of excited states. During the past twenty years, fine particles of organic compounds were prepared by reprecipitation method, and their optical properties have been studied (Kasai et al., 1992, 1995, 1996, Katagi et al.). Recently organic phosphorescent nanoparticles were reported (Miyashita et al.).

Luminescent semiconductor nanoparticles have been used for bioimaging (Web-1). However, they contain heavy metals or toxic elements. Development of luminescent organic nanoparticles is strongly expected for bioimaging application, because organic nanoparticles will be much less toxic than semiconductor ones.

We have already reported two-photon absorption cross sections of nanoparticles of naphthalocyanine derivatives (Takemura et al.), third-order nonlinear optical properties of several organic nanoparticles (Kasatani et al., 2009), and fluorescence behavior of organic nanoparticles, mainly of anthracene nanoparticles (Kasatani et al., 2011). In this study, we measured UV/visible absorption spectra, fluorescence spectra, fluorescence quantum yields, and fluorescence lifetimes, of nanoparticles of anthracene and 1,4-bis(2-methylstyryl)benzene (bis-MSB). Fluorescence quantum yields of both anthracene nanoparticles doped with naphthacene and anthracene nanoparticles doped with perylene were as high as 0.75.

2. EXPERIMENTAL

Figure 1 shows structural formulas of organic compounds studied. Anthracene and bis-MSB were used as nanoparticles, and naphthacene and perylene were used as dopants. These compounds were purified several times by recrystalization. Transparent organic nanoparticles dispersed in water were prepared by reprecipitation method. The typical condition for preparing anthracene nanoparticles was as follows: 1 ml of acetone solution of anthracence (ca. 2×10^{-3} M) was injected using a syringe into 100 ml of water stirred vigorously at ca. 10^{o}C. A dopant (naphthacene or perylene) was added in acetone solutions at a very low concentration. Poly(vinyl alcohol) (PVA, 100 ppm) was added to the water to stabilize nanoparticles in water.

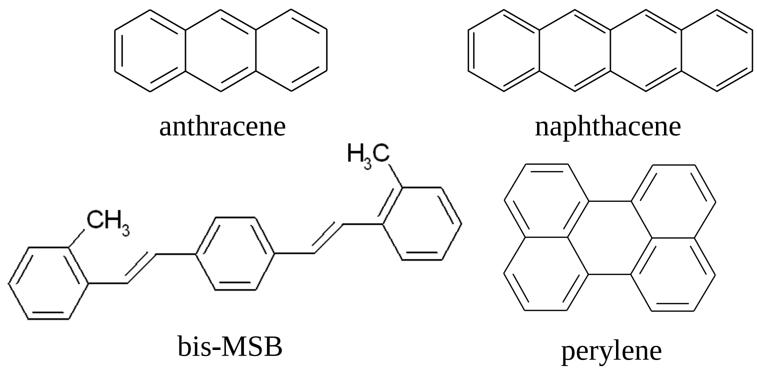

Figure 1: Structural formulas of organic compounds studied.

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 to be a double exponential function

$$R(t) = \mathrm{a}_1\exp(-\mathrm{t}/\mathrm{t}_1) + \mathrm{a}_2\exp(-\mathrm{t}/\mathrm{t}_2) \qquad (2)$$

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 (Marquardt, O'Connor et al.). Scattered light of a laser pulse is recorded as L(t).

3. RESULTS AND DISCUSSION

Figures 2 and 3 show the UV/visible absorption spectra of anthracene nanoparticles and those of bis-MSB nanoparticles, respectively. A very small amount of dopant gave no influence on the absorption spectra of both matrixes. Doping anthracene nanoparticles with naphthacene does not change UV/visible absorption spectra because of the very low concentration of the dopant.

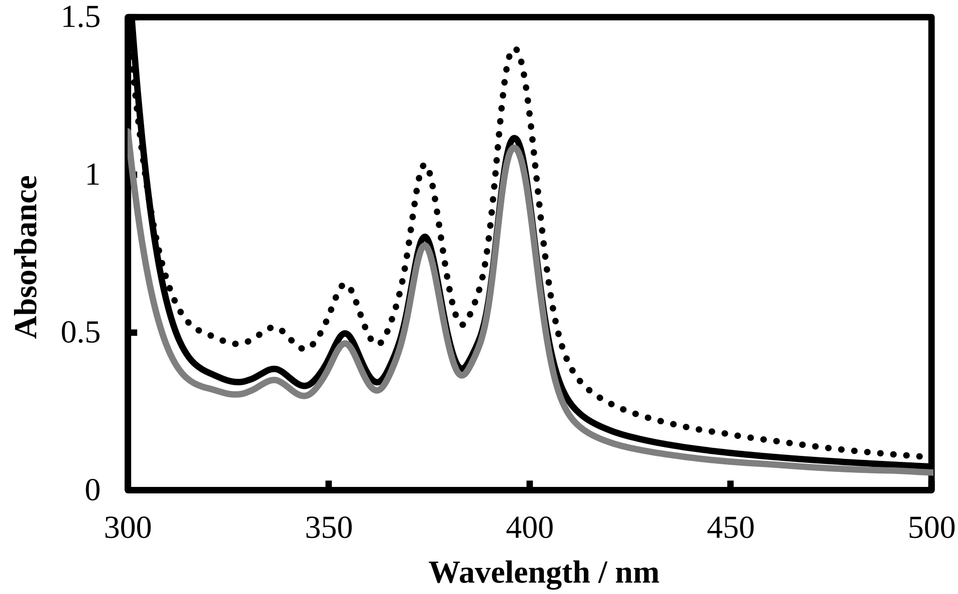

Figure 2: Ultraviolet/visible absorption spectrum of anthracene nanoparticles (black solid line), that of anthracene nanoparticles doped with perylene (black dotted line), and that of anthracene nanoparticles doped with naphthacene (gray solid line).

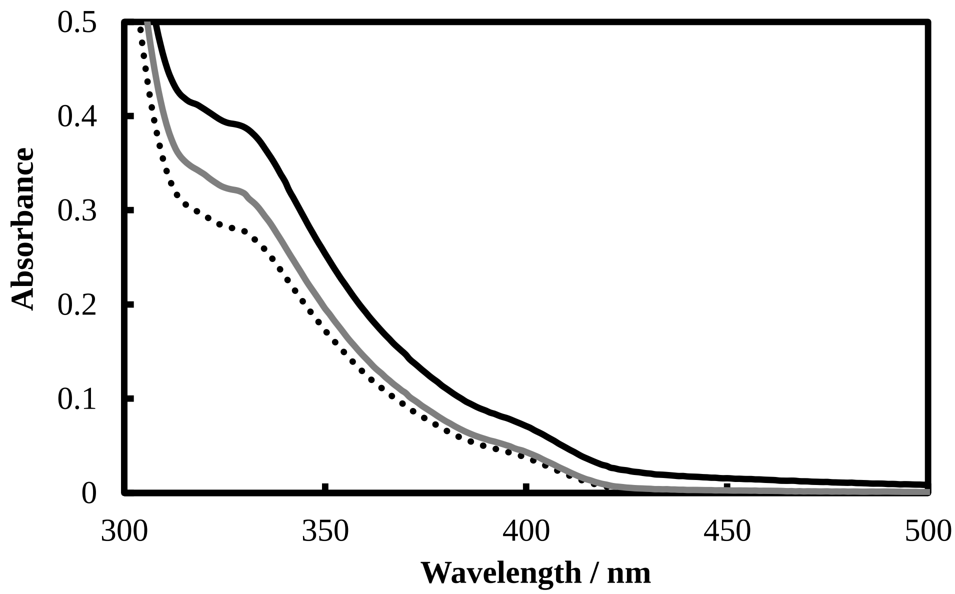

Figure 3: Ultraviolet/visible absorption spectrum of bis-MSB nanoparticles (black solid line), that of bis-MSB nanoparticles doped with perylene (black dotted line), and that of bis-MSB nanoparticles doped with naphthacene (gray solid line).

Figure 4 shows fluorescence spectra of anthracene nanoparticles doped with naphthacene. Exciting wavelength was 375 nm. The fluorescence spectrum of anthracene nanoparticles without dopant shows fluorescence longer than ca. 400 nm with a weak vibronic structure. Doping of naphthacene decreased fluorescence of anthracene nanoparticles and strong fluorescence of naphthacene appeared. Fluorescence of anthracene nanoparticles almost disappeared at a doping concentration of as low as 0.1 mol%.

Figure 5 shows fluorescence spectra of anthracene nanoparticles doped with perylene. Exciting wavelength was 375 nm. Doping of perylene decreased fluorescence of anthracene nanoparticles and strong fluorescence of perylene appeared. Fluorescence of anthracene nanoparticles almost disappeared at a doping concentration of 0.1 mol%.

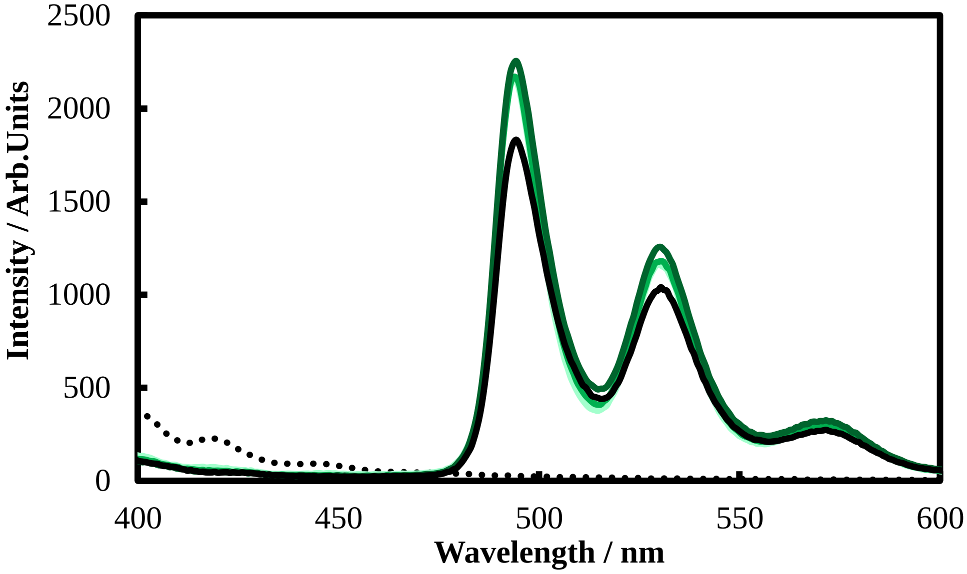

Figure 4: Fluorescence spectra of anthracene nanoparticles and anthracene nanoparticles doped with naphthacene. Concentration of naphthacene: 0 mol% (black dotted line), 0.1 mol% (lightt green solid line), 0.3 mol% (green solid line), 0.5 mol% (dark green line), 0.7 mol% (black solid line).

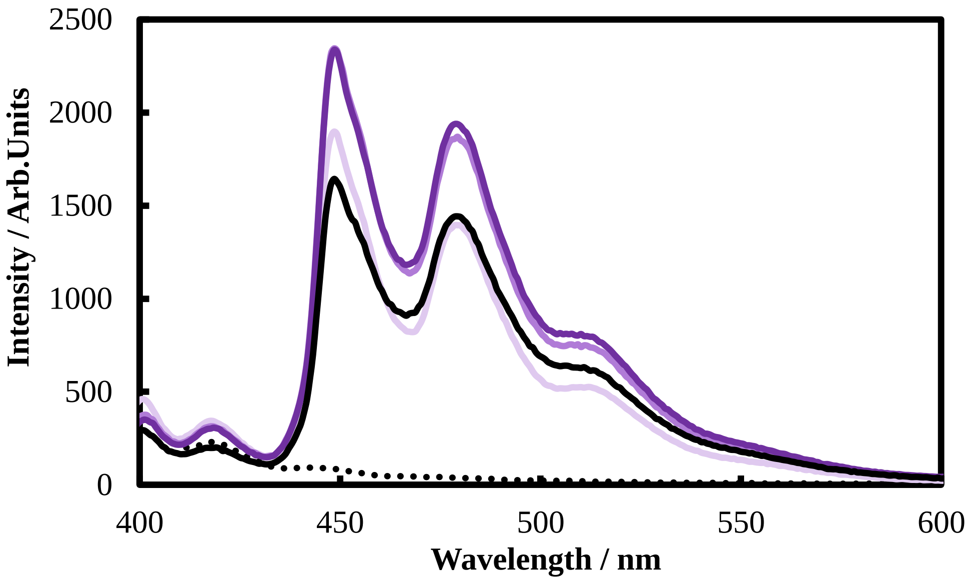

Figure 5: Fluorescence spectra of anthracene nanoparticles and anthracene nanoparticles doped with perylene. Concentration of perylene: 0 mol% (black dotted line), 0.1 mol% (light purple dotted line), 0.3 mol% (purple solid line), 0.5 mol% (dark purple solid line), 0.7 mol% (black solid line).

Figure 6 shows fluorescence spectra of bis-MSB nanoparticles doped with naphthacene. Exciting wavelength was 375 nm. The fluorescence spectrum of bis-MSB nanoparticles without dopant shows fluorescence longer than 420 nm. Doping of naphthacene decreased fluorescence of bis-MSB nanoparticles and strong fluorescence of naphthacene appeared. Fluorescence of bis-MSB nanoparticles almost disappeared at a doping concentration of 4 mol%.

Figure 7 shows fluorescence spectra of bis-MSB nanoparticles doped with perylene. Exciting wavelength was 375 nm. Doping of perylene decreased fluorescence of bis-MSB nanoparticles and strong fluorescence of perylene appeared. Fluorescence of bis-MSB nanoparticles almost disappeared at a doping concentration of 0.5 mol%.

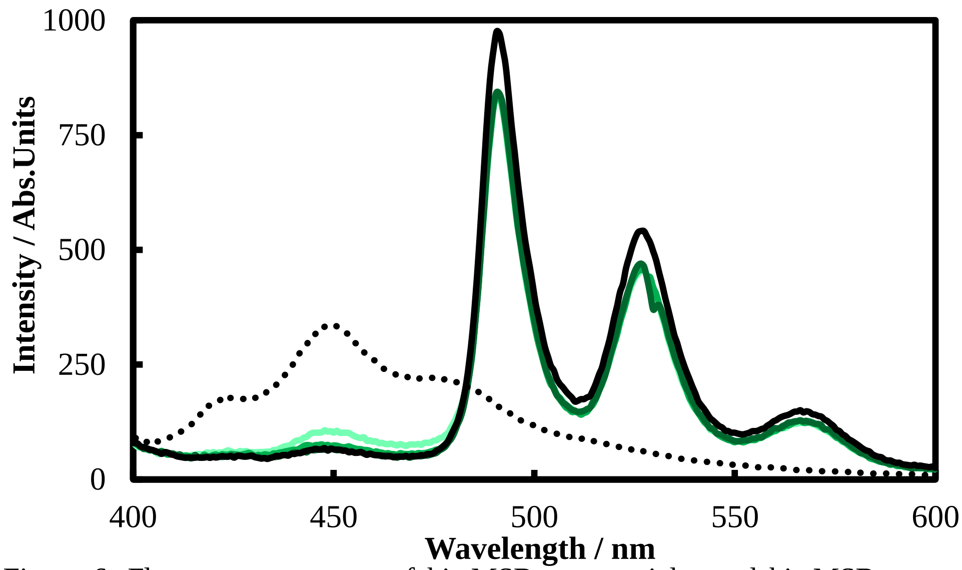

Figure 6: Fluorescence spectra of bis-MSB nanoparticles and bis-MSB nanoparticles doped with naphthacene. Concentration of naphthacene: 0 mol% (black dotted line), 4 mol% (light green line), 6 mol% (green solid line), 8 mol% (darkt green solid line), 10 mol% (black solid line).

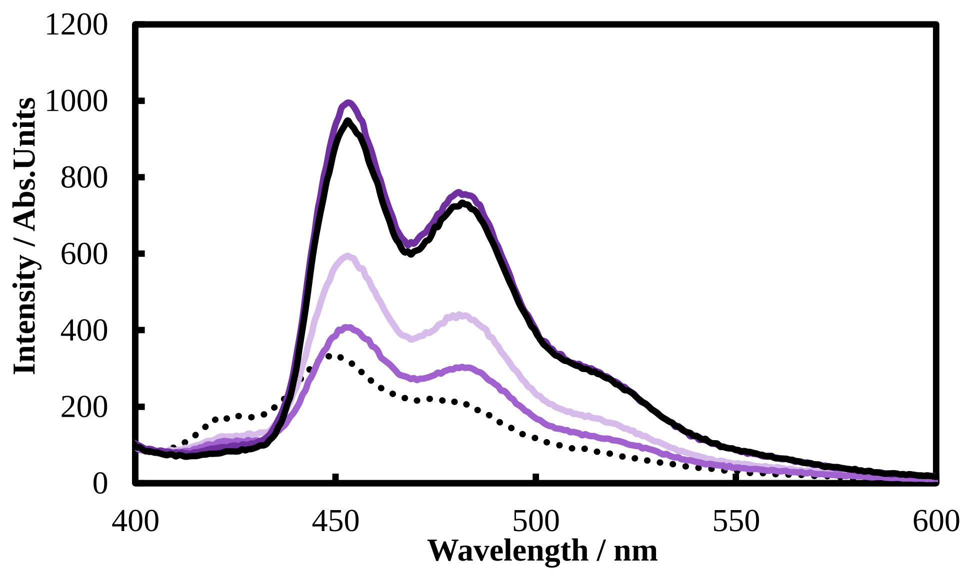

Figure 7: Fluorescence spectra of bis-MSB nanoparticles and bis-MSB nanoparticles doped with perylene. Concentration of perylene: 0 mol% (black dotted line), 0.5 mol% (the lightest purple dotted line), 1.0 mol% (purple solid line), 1.5 mol% (dark purple solid line), 2.0 mol% (black solid line).

Figures 8 and 9 show the dependences of fluorescence quantum yield on doping concentration for anthracene nanoparticles doped with naphthacene and anthracene nanoparticles doped with perylene, respectively. Fluorescence quantum yield of anthracene nanoparticles increased drastically from 0.10 by doping. The largest value of fluorescence quantum yield of anthracene nanoparticles doped with naphthacene was as high as 0.75 at a naphthacene concentration of 0.5 mol%. The largest value of fluorescence quantum yield of anthracene nanoparticles doped with perylene was also as high as 0.75 at a perylene concentration of 0.25 mol%.

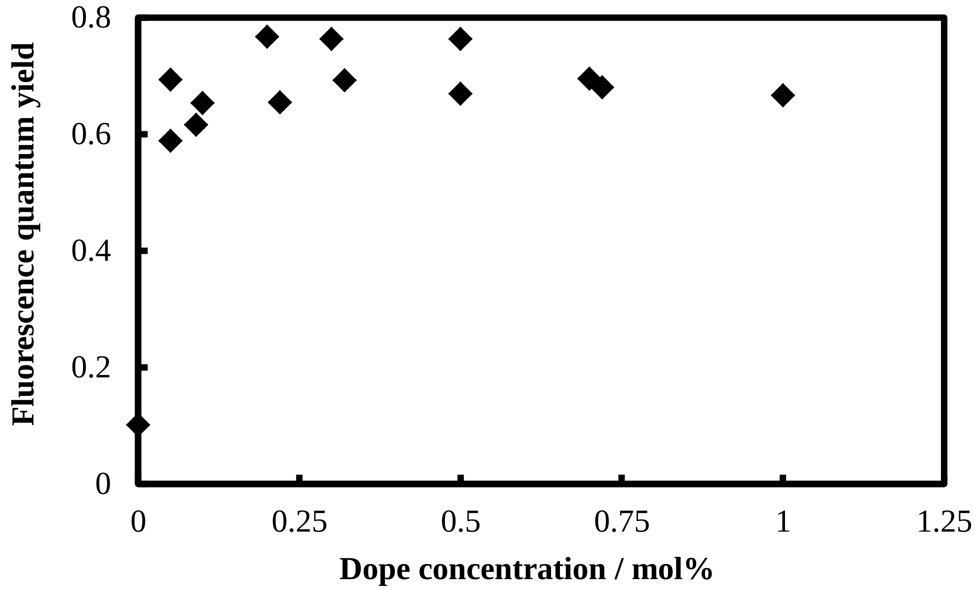

Figure 8: The dependence of fluorescence quantum yield of anthracene nanopariticles doped with naphthacene on dopant concentration.

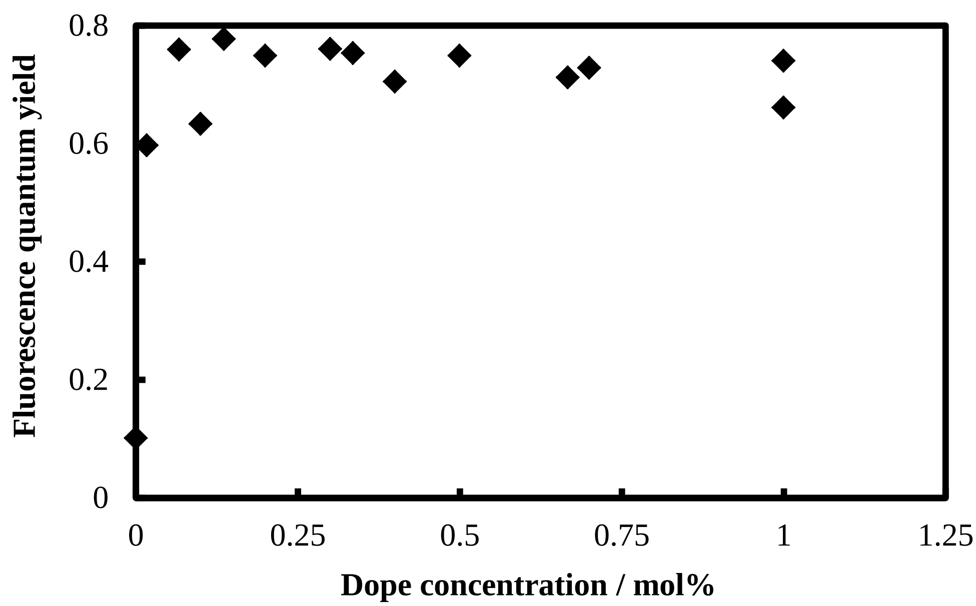

Figure 9: The dependence of fluorescence quantum yield of anthracene nanopariticles doped with perylene on dopant concentration.

Figures 10 and 11 show the dependences of fluorescence quantum yield on doping concentration for bis-MSB nanoparticles doped with naphthacene and bis-MSB nanoparticles doped with perylene, respectively. Fluorescence quantum yield of bis-MSB nanoparticles increased from 0.15 by doping. The largest value of fluorescence quantum yield of bis-MSB nanoparticles doped with naphthacene was about 0.35 at a naphthacene concentration of 7.5 mol%. The largest value of fluorescence quantum yield of bis-MSB nanoparticles doped with perylene was about 0.55 at a perylene concentration of 2.0 mol%.

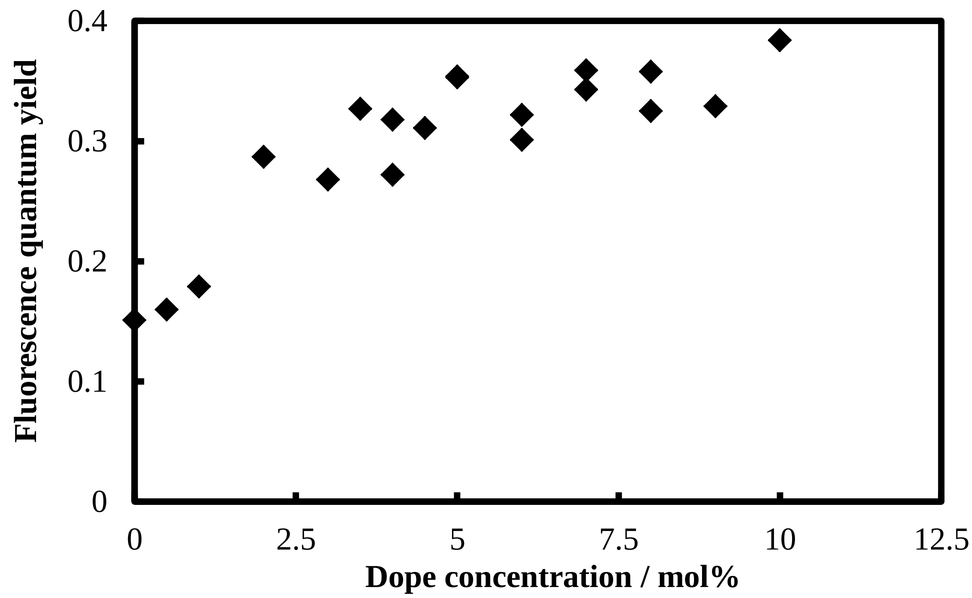

Figure 10: The dependence of fluorescence quantum yield of bis-MSB nanopariticles doped with naphthacene on dopant concentration.

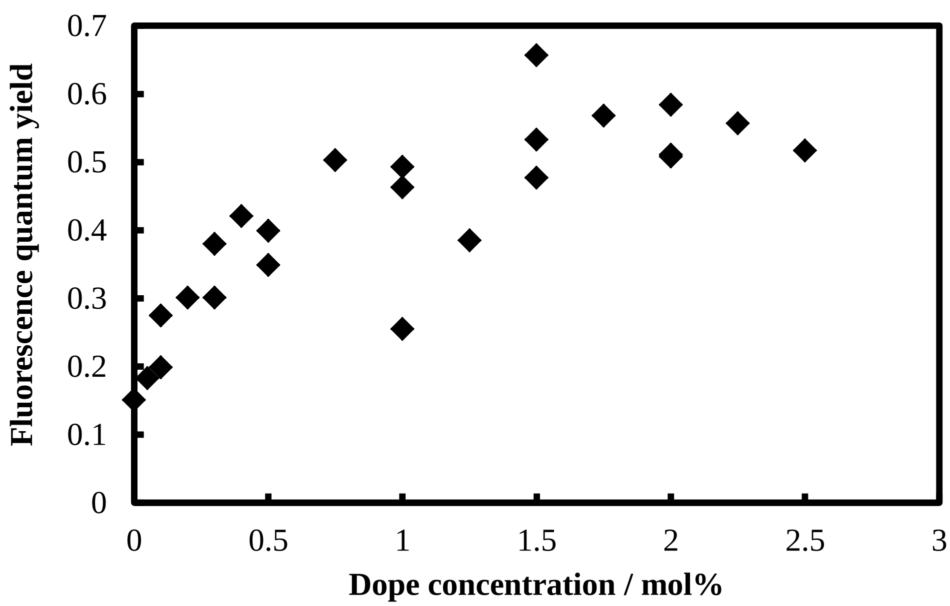

Figure 11: The dependence of fluorescence quantum yield of bis-MSB nanopariticles doped with perylene on dopant concentration.

Fluorescence decay curve of anthracene nanoparticles doped with naphthacene was single exponential (see Fig. 12). On the other hand, fluorescence decay curve of anthracene nanoparticles doped with perylene was not single exponential (see Fig. 13). We assumed double exponential response for the fluorescence of these nanoparticles. The results of all lifetime measurements are summarized in Tables 1-4.

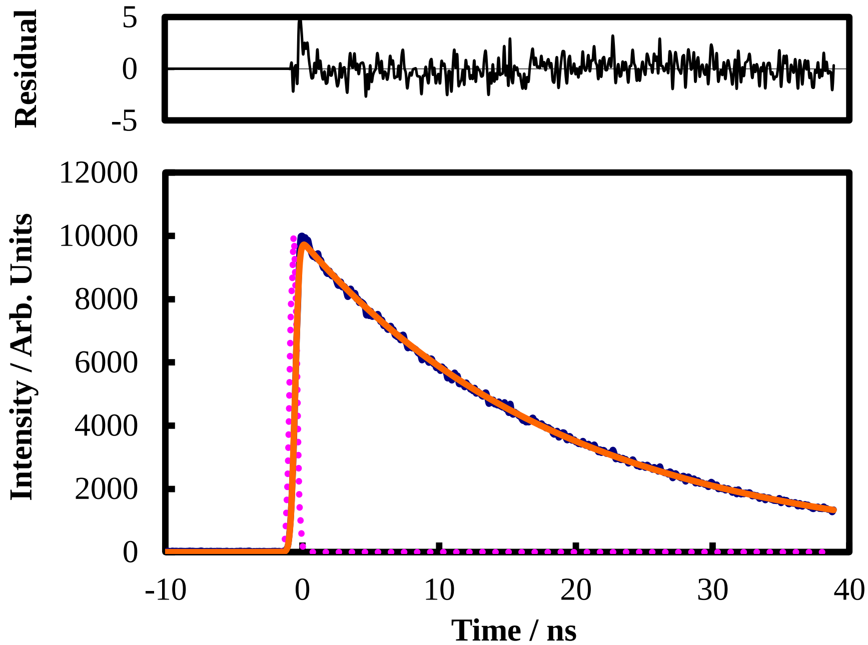

Figure 12: Fluorescence decay curve of anthracene nanoparticles doped with naphthacene and its simulation. The dope concentration of naphthacene: 0.5mol%. Fluorescence intensity (dark blue solid line), laser (pink dotted line), simulation (orange solid line).

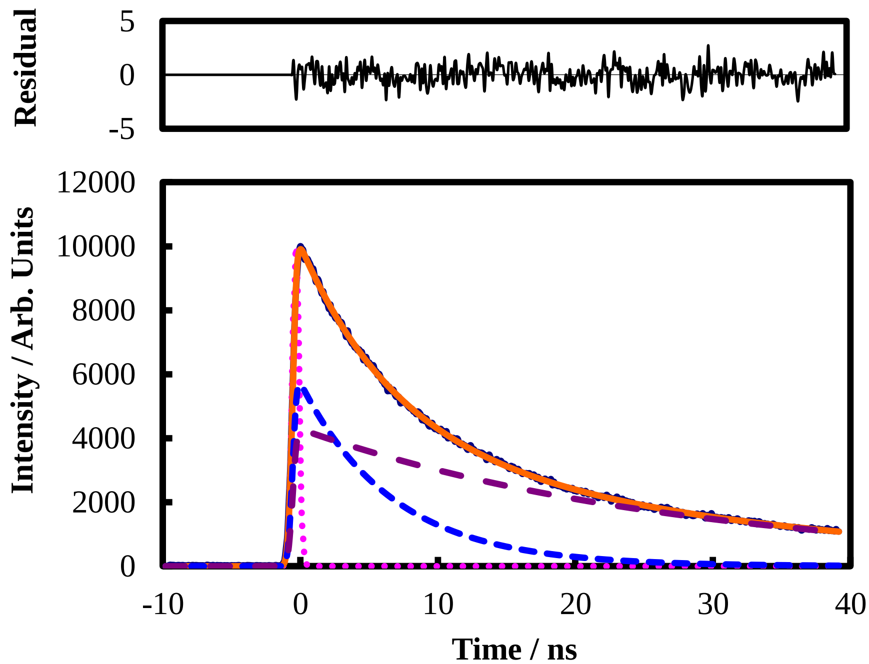

Figure 13: Fluorescence decay curve of anthracene nanoparticles doped with peylene and its simulation. The dope concentration of perylene: 0.5mol%. Fluorescence intensity (dark blue solid line), laser (pink dotted line), simulation (orange solid line), first exponential (blue dotted line), second exponential (dark red broken line).

On comparison between the results of anthracene nanoparticles doped with naphthacene and those of bis-MSB nanoparticles doped with naphthacene, we concluded that anthracene nanoparticles are good matrices for naphthacene; fluorescence quantum yields were higher and fluorescence lifetimes were longer in anthracene nanoparticles than in bis-MSB nanoparticles. Doping efficiency of naphthacene into bis-MSB nanoparticles seems very poor; probably high percentage of naphthacene cannot be doped into bis-MSB nanoparticles. For perylene, anthracene nanoparticles are also better matrices than bis-MSB nanoparticles. However, high doping concentration into anthracene nanoparticles induced concentration quenching; dimer formation in a nanoparticle may have reduced fluorescence quantum yield at high dope concentration. In all four kinds of doped nanoparticles, energy transfer from a nanoparticle to a dopant molecule seems to be very fast and effective.

Table 1: Fluorescence lifetimes of anthracene nanoparticles doped with naphthacene

concentration of naphthacene / mol%	Fluorescence lifetime / ns	
	Fast(Weight)	Slow(Weight)
0	1.83 (94.1%)	15.3 (5.9%)
0.25	21.1(-)	-(-)
0.50	19.3(-)	-(-)
1.00	0.44 (15.8%)	17.3 (84.2%)

Table 2: Fluorescence lifetimes of anthracene nanoparticles doped with perylene

concentration of perylene / mol%	Fluorescence lifetime / ns	
	Fast(Weight)	Slow(Weight)
0	1.83 (94.1%)	15.3 (5.9%)
0.25	8.71 (61.8%)	33.7 (38.2%)
0.50	6.68 (58.7%)	28.0 (41.3%)
1.00	5.77 (56.8%)	22.2 (43.2%)

Table 3: Fluorescence lifetimes of bis-MSB nanoparticles doped with naphthacene

concentration of perylene / mol%	Fluorescence lifetime / ns	
	Fast(Weight)	Slow(Weight)
0	1.23 (81.9%)	5.72 (18.1%)
2.00	1.01 (25.3%)	17.5 (74.7%)
5.00	3.87 (16.4%)	17.6 (83.6%)
8.00	3.55 (18.6%)	17.0 (81.4%)

Table 4: Fluorescence lifetimes of bis-MSB nanoparticles doped with perylene

concentration of naphthacene / mol%	Fluorescence lifetime / ns	
	Fast(Weight)	Slow(Weight)
0	1.23 (81.9%)	5.72 (18.1%)
0.10	3.49 (56.1%)	11.1 (43.9%)
1.00	3.07 (57.9%)	10.5 (42.1%)
2.00	3.79 (58.4%)	11.7 (41.6%)

4. CONCLUSIONS

Fluorescence spectra, fluorescence quantum yields, and fluorescence lifetimes of anthracene nanoparticles doped with perylene, anthracene nanoparticles doped with naphthacene, bis-MSB nanoparticles doped with perylene, and bis-MSB nanoparticles doped with naphthacene, were measured. When doping nanoparticles with a dopant, fluorescence of nanoparticles was quenched and strong fluorescence of dopant was observed. Energy transfer from a nanoparticle to a dopant molecule was fast and efficient. Fluorescence quantum yields of both anthracene nanoparticles doped with naphthacene and anthracene nanoparticles doped with perylene were as high as 0.75 Fluorescence quantum yields of bis-MSB nanoparticles doped with naphthacene and that of bis-MSB nanoparticles doped with perylene were about 0.35 and about 0.55, respectively.

5. ACKNOWLEDGMENTS

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