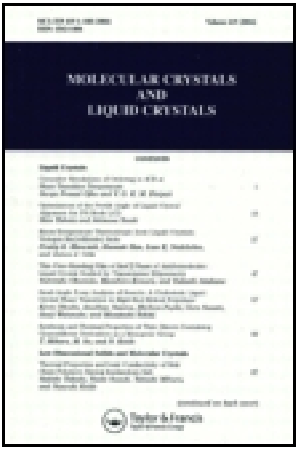

Molecular Crystals and Liquid Crystals

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Optical Properties of 1-Phenyl-3-Naphthyl-5-((Ethoxy)phenyl)-2-Pyrazoline Organic Nanoparticlesby Reprecipitation Method

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Optical Properties of 1-Phenyl-3-Naphthyl-5-((Ethoxy)phenyl)-2-Pyrazoline Organic Nanoparticles by Reprecipitation Method

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Nanoparticles of 1-phenyl-3-naphthyl-5-((ethoxy)phenyl)-2-pyrazoline with sizes ranging from tens to hundreds of nanometers were prepared by the reprecipitation method. Their excitonic transitions responsible for absorption and emission, as compared with those of diluted solution, have been investigated as a function of nanoparticle size. We found that pyrazoline nanoparticles possess an ambiguous size dependence on their optical properties. As the nanoparticle size decreased, the absorption peak of pyrazoline nanoparticles was observed to be shifted to the high-energy side due to size effect.

Keywords: organic nanoparticles; pyrazoline; reprecipitation method; size-dependent

INTRODUCTION

Nanoparticles of semiconductors have been an extremely active area of research because of their quantum effect on optical and electronic properties [1]. However, studies of organic nanoparticles have been paid little attention. In case of organic molecular crystals, their electronic and optical properties are fundamentally different from

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those of inorganic metals and semiconductors, due to weak intermolecular interaction forces of the van der Waals type [2].

As far as the application is concerned, organic nanoparticles are expected to hold the higher potentials because organic nanoparticles allow much more variability and flexibility in materials synthesis and nanoparticle preparation. Investigations on the organic nanoparticles, however, are only at their very initial stages presently. Pyrazolines have been widely used as optical brightening agents for textiles and fabrics as a hole-conveying medium in photoconductive materials [2–5]. Specially 2-pyrazolines containing electron donors and acceptors at 1- and 3-positions were a typical heterocyclic 'transition' molecular crystal and have a large molecular hyperpolarizability which suggests the photorefractivity of two-dimensional-array constructed.

In this study, nanoparticles of 1-phenyl-3-naphthyl-5 -((ethoxy)phenyl)-2-pyrazoline with sizes ranging from tens to hundreds of nanometers have been successfully prepared by the reprecipitation method, and their size-dependent optical properties have been studied.

EXPERIMENTAL

Materials

4-((Ethoxy)phenyl)aldehyde, sodium ethoxide, 2′-acetonaphthone and phenylhydrazine were purchased from Aldrich Chemical Co. All solvents were obtained from Junsei Chemical Co. House-distilled water was passed through a four-cartridge Barnstead Nanopure II purification system consisting of macropure pretreatment, organic-free (for removing trace organics), two-ion exchangers and 0.2 mm hollow-fiber final filter for removing particles.

Preparation of 1-Phenyl-3-Naphthyl-5-((Ethoxy)phenyl)-2-Pyrazoline

Synthetic Route of 1-phenyl-3-naphthyl-5-((ethoxy)phenyl)-2-pyrazoline is summarized in Figure 1. To a solution of 4-((ethoxy)phenyl)) aldehyde (14.9 g, 0.10 mol) in 300 mL of ethanol was added sodium ethoxide (21 wt% solution in ethanol, 37.3 mL) and stirred for 1 h at 25°C. To a solution was added 2′-acetonaphthone (17.0 g, 0.10 mol) and stirred for 24 h at 25°C. The precipitate was filtered, washed with water and recrystallized with benzene to yield 24.1 g (80%) of chalone 1. ^{1}H-NMR ($CDCl_3$) 1.45 (t, 3 H, $J = 8.0$ Hz, CH_3), 4.10 (q, 2 H, $J = 8.0$ Hz, CH_2), 6.95 (2 H, d, $J = 8.0$ Hz, CH=CH), 7.56–7.66

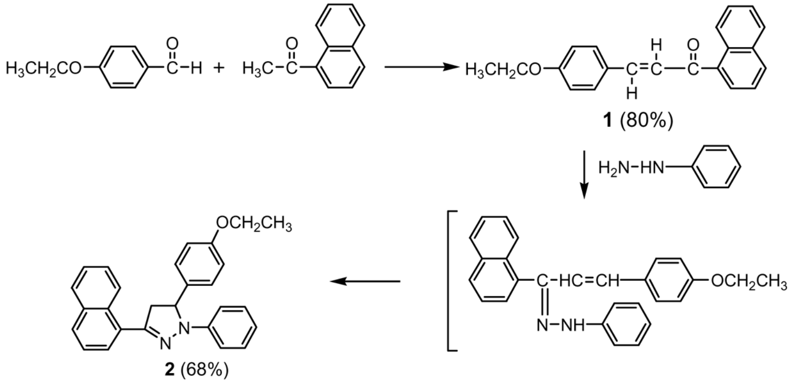

FIGURE 1 The synthetic route of 1-phenyl-3-naphthyl-5-((ethoxy)phenyl)-2-pyrazoline.

(m, 5H, aromatic), 7.84–7.95 (m, 3 H, aromatic), 8.00 (1 H, d, $J = 8.0$ Hz, aromatic), 8.10 (dd, 1 H, $J = 8.0$ Hz and $J = 1.6$ Hz, aromatic), 8.53 (s, 1 H, aromatic). ^{13}C-NMR ($CDCl_3$) 14.6 (CH_3), 65.5 (CH_2), 114.8 and 119.5 (CH=CH), 124.4, 126.6, 127.4, 127.7, 127.9, 128.1, 128.4, 129.4, 129.6, 129.8, 130.2, 132.5, 135.3, 135.8, 144.6 and 161.2 (aromatic), 190.1 (C=O).

A solution of 1 (5.0 g, 16.6 mmol) and phenylhydrazine (1.98 g, 18.3 mmol) in 50 mL of acetic acid was heated for 4 h at 100°C and then cooled to room temperature. The precipitate was filtered, washed with ethanol and recrystallized with benzene to yield 4.4 g (68%) of pyrazoline 2. ^{1}H-NMR ($CDCl_3$) 1.39 (t, 3 H, $J = 7.0$ Hz, CH_3), 3.25 (dd, 1 H, $J = 7.2$ Hz and $J = 13.9$ Hz, $NCHC\underline{H}_2$), 3.92 (dd, 1 H, $J = 12.4$ Hz and $J = 16.9$ Hz, $NCHC\underline{H}_2$), 4.00 (q, 2 H, $J = 7.0$ Hz, OCH_2), 5.29 (dd, 1 H, $J = 7.1$ Hz and $J = 12.2$ Hz, NCH), 6.08 (t, 1 H, $J = 7.1$ Hz, aromatic), 6.84–6.88 (m, 2 H, aromatic), 7.13 (d, 2 H, $J = 7.5$ Hz, aromatic), 7.18–7.27 (m, 4 H, aromatic), 7.46–7.48 (m, 2 H. aromatic), 7.79–7.85 (m, 4 H, aromatic), 8.18 (dd, 2 H, $J = 1.6$ Hz and $J = 8.9$ Hz, aromatic) ^{13}C-NMR ($CDCl_3$) 14.8 (CH_3), 43.5 ($NCH\underline{C}H_2$), 63.4 (NCH), 64.1 (OCH_2), 123.5, 124.2, 124.7, 125.0, 125.5, 126.0, 126.2, 126.3, 126.4, 127.0, 127.6, 127.8, 128.0, 128.1, 128.3, 128.9, 129.0, 130.0, 130.5, 133.3, 133.4, and 134.4 (aromatic), 158.4 (C=N)

Methods

The ^{1}H-NMR and ^{13}C-NMR spectra were recorded using 400 MHz spectrometers (Varian). All compounds in purities are greater than

90% as judged by ^{1}H-NMR and ^{13}C-NMR. The size and shape of nanoparticles were observed by means of transmisson electron microscope (TEM: Hitachi S-2400, Japan). The UV-vis optical absorption spectra of nanoparticle dispersed in water were measured using a Varian Carry UV–vis spectrophotometer. The excitation and emission fluorescence spectra were recorded with a fluorescence spectrometer (Hitachi F-4500).

Preparations of Pyrazoline Nnoparticles

1-Phenyl-3-naphthyl-5-((ethoxy)phenyl)-2-pyrazoline (2) nanoparticles were prepared as follows. Pyrazoline acetone solution (1.0 mM) was injected into 10 mL of water with vigorous stirring, using a 100 μL microsyringe. Pyrazoline molecules began to be aggregated at once and its nanoparticles dispersed in water were obtained. By controlling the quantity of pyrazoline acetone solution injected into water and temperature, the size of nanoparticles was controlled. For example, when 100 and 50 μL of pyrazoline acetone solution were injected, the nanoparticle sizes finally prepared were 65 and 40 nm at 25°C, respectively.

RESULTS AND DISCUSSION

We successfully prepared a series of pyrazoline (2) nanoparticles from tens to hundreds nanometers. Some of their TEM images are shown in Figure 2, in which the average nanoparticle sizes were 20, 40, 90, 120 and 140 nm ± 5 nm, respectively. As the size increased, the shape of pyrazoline nanoparticles was changed from sphere to cubic. This change of shape can be explained by the formation of aggregate.

Figure 3 displays the UV-visible absorption spectra of pyrazoline (2) nanoparticles dispersed into water with different size and the spectrum of pyrazoline (2) acetone solution (1.0×10^{-2} mM). As the particle size decreases from 130 to 40 nm, $\lambda_{\max}$ of pyrazoline (2) nanoparticles was shifted to a shorter wavelength region. It is interpreted as the more electron delocalization on the main backbone gets $\lambda_{\max}$ to be shifted to a longer wavelength. This indicates that the size-dependent property of pyrazoline (2) nanoparticles is completely different from single pyrazoline (2) molecule. In Figure 3, we observed that the absorption peak is strongly affected by the nanoparticle sizes. It is expected for an aggregate state arising from the π-π orbital overlap of closely stacked pyrazoline molecules in nanoparticles and is similar to the pervious observations of absorption by aggregate states in other organic molecular crystals such as α-perylene [6] and tetracene [7,8].

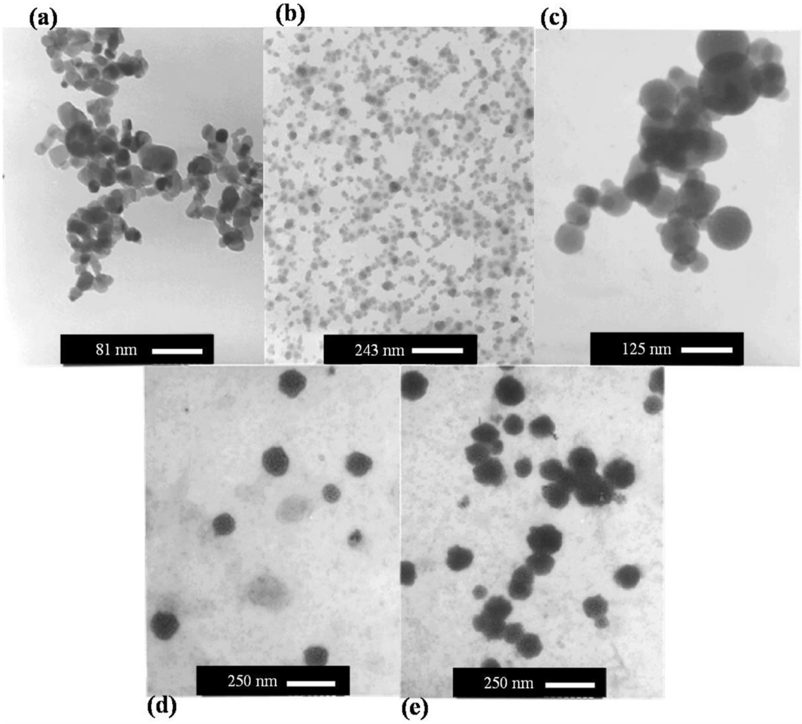

FIGURE 2 TEM images of 1-phenyl-3-naphthyl-5-((ethoxy)phenyl)-2-pyrazoline nanoparticles (a: 20 nm, b: 40 nm, c: 90 nm, d: 120 nm, e: 140 nm ± 5 nm).

As it is already known by Nakanishi, the reason of size-dependent property is the change of lattice state due to the increase of the surface area. It is likely that the increase of the surface area causes lattice softening, the Coulombic interaction energies between molecules become smaller, leading to wider band gap.

Figure 4 displays the fluorescence emission spectra of pyrazoline (2) nanoparticles with different sizes, compared with those of the dilute acetone solution. With increasing nanoparticle size, the peak was shifted to the longer wavelength region. In Figure 4, the shape of the nanoparticle emission spectrum is similar to that of the dilute solution, and its peak shifts to the longer wavelength region from the dilute solution. The shift of peak is close to the energy difference between absorption transitions from S_o to high vibrational levels ($\nu_n = 0,\ldots,n$) of S_1 (labeled [$S_o(0)$–$S_1(n)$]).

Thus, the nanoparticle emission peak is from $S_1(n)$ to $S_o(0)$. The emission spectra indicates that, in nanoparticles, the energy space

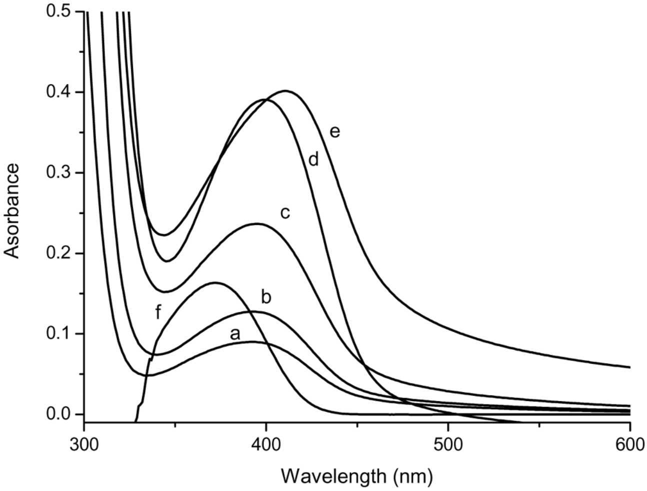

FIGURE 3 UV-vis Spectra of water dispersion of pyrazoline nanoparticles with different sizes; (a) 20, (b) 40, (c) 90, (d) 120, (e) 140 nm, (f) the spectrum of pyrazoline acetone solution (1.0×10^{-2} mM).

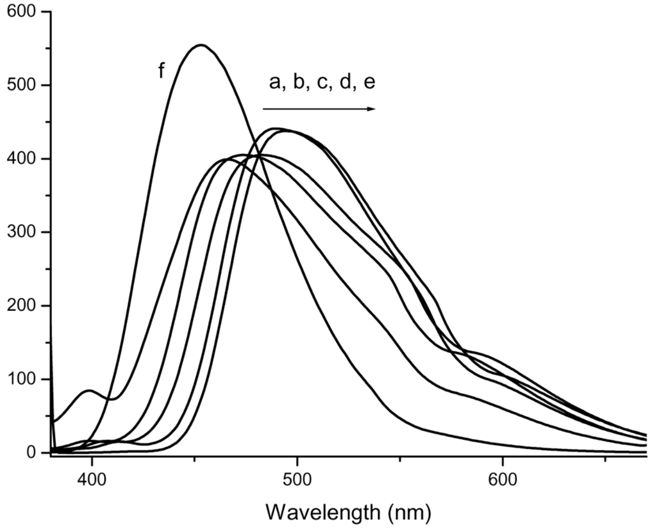

FIGURE 4 Fluorescence emission spectra of water dispersion of pyrazoline nanoparticles with different sizes; (a) 20, (b) 40, (c) 90, (d) 120, (e) 140 nm, (f) the spectrum of pyrazoline acetone solution (1.0×10^{-2} mM).

between $S_1(n)$ and $S_o(0)$ decreases with increasing nanoparticle size. In the investigation of the fabrication of organic nanoparticle using pyrazoline derivative, the size-dependent optical properties have been observed by a change of electron donating functional group at 5-positon. The emission color can be modulated by the nanoparticle size. In this study, the size-dependence of absorption and emission exhibited by pyrazoline (2) nanoparticles is due to the aggregate formation and increased intermolecular interaction.

CONCLUSIONS

1-Phenyl-3-naphthyl-5-((ethoxy)phenyl)-2-pyrazoline (2) nanoparticles with different size were prepared by the reprecipitation method. We found that the particle size plays a critical role in optical properties of organic nanoparticles. These optical properties of the organic nanoparticles as a function of particle size are useful for controlling the color of the light emitted for electroluminescent materials only by the variation of the particle size.

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