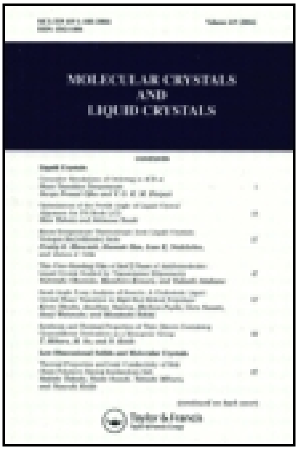

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

The size-dependent optical properties of pyrazoline nanoparticles

Sun Oh [a] & Young Kang [b]

[a] Basic Science Research Institute, Pukyong National University, Pusan, Korea

[b] Department of Chemistry, Pukyong National University, Pusan, Korea

To cite this article: Sun Oh & Young Kang (2004): The size-dependent optical properties of pyrazoline nanoparticles, Molecular Crystals and Liquid Crystals, 425:1, 205-212

To link to this article: http://dx.doi.org/10.1080/15421400490506838

Mol. Cryst. Liq. Cryst., Vol. 425, pp. 205/[483]–212/[490], 2004
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490506838

THE SIZE-DEPENDENT OPTICAL PROPERTIES OF PYRAZOLINE NANOPARTICLES

Sun Wha Oh
Basic Science Research Institute, Pukyong National University,
Pusan 608-737, Korea

Young Soo Kang
Department of Chemistry, Pukyong National University,
Pusan 608-737, Korea

Organic nanoparticles of 1-phenyl-3-naphthyl-5-((dimethylamino)phenyl)-2-pyrazoline were prepared by the reprecipitation method. Their excitonic transitions responsible for absorption and emission, as compared with those of dilute solution, have been investigated as a function of nanoparticle size. We found that pyrazoline nanoparticles possess a special size dependence in their optical properties. As the nanoparticle size decreased, the absorption and emission peak of pyrazoline nanoparticles were observed to shift to the high-energy side due to size effect.

Keywords: nanoparticles; optical properties; reprecipitation method; size effect

INTRODUCTION

In recent years, the number of studies of organic nanoparticles has been increasing. Because of the diversity of organic molecules, there is a tendency to extend the research on nanoparticles from metals and semiconductors into organic field, especially into general organic molecules [1,2]. In case of organic molecular crystals, their electronic and optical properties are fundamentally different from those of inorganic metals and semiconductors, due to weak intermolecular interaction forces of the van der Waals

---

Received 1 October, 2003; accepted 6 January, 2004.
This work was supported by Korea Research Foundation Grant (KRF-2002-050-C00007).

Address correspondence to Young Soo Kang, Department of Chemistry, Pukyong National University, Busan, 608-737, Korea. Tel.: +82-51-620-6379, Fax.: +82-51-628-8147, E-mail: yskang@pknu.ac.kr

type [3]. To understand how these properties develop as a function of size is fundamental and technological interest.

Inorganic semiconductor or metal nanoparticles have been extensively investigated for various potential applications including the fluorescent biological labels [4], photovoltaic cells [5], light emitting diodes [6], and optical sensors [7]. 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 material synthesis and nanoparticle preparation. Investigations on the organic nanoparticles, however, are only at their very initial stages presently. Recently, Yao *et al.*, reported that pyrazoline nanoparticles show very different and size-dependent properties from those of bulk samples [8–11].

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

EXPERIMENTAL

Materials

4-(Dimethylamino)aldehyde, sodium ethoxide, 2′-acetonaphthone and phenylhydrazine were purchased from Aldrich Chemical Co. and used without any further purification. All solvents were obtained from Junsei Chemical Co. and used without further purification. 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. Its resistivity was 18.3 MΩ and used in all the experiments.

Preparations of Pyrazoline Nanoparticles

1-Phenyl-3-naphthyl-5-((dimethylamino)phenyl)-2-pyrazoline nanoparticle was synthesized according to the previous report and conformed by NMR and MS [12]. Its molecular structure is shown in Figure 1. 1-Phenyl-3-naphthyl-5-((dimethylamino)phenyl)-2-pyrazoline 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

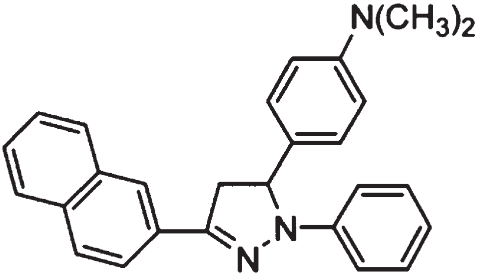

FIGURE 1 The molecular structure of 1-phenyl-3-naphthyl-5-((dimethylamino) phenyl)-2-pyrazoline.

nanoparticles was controlled. For example, when 100 and 50 μL of pyrazoline acetone solution were injected, the nanoparticle sizes finally prepared were determined as 65 and 40 nm at 25°C, respectively.

Methods

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). The size and shape of nanoparticles were observed by means of the transmission electron microscope (TEM: Hitachi S-2400, Japan). The size and distribution of nanoparticles dispersed in water were also evaluated by the dynamic light scattering (DLS) technique using a Zetaplus 1246 (Brookhaven Instruments Corporation, USA).

RESULTS AND DISCUSSION

We successfully prepared a series of pyrazoline nanoparticles from tens to hundreds nanometers, which were stable even after several weeks. Some of their TEM images are shown in Figure 2, in which the average nanoparticle sizes were determined as 40, 65, 90 and 130 nm, respectively. TEM images also showed that the size distribution of pyrazoline nanoparticles tends to be uniform as confirmed by DLS.

Figure 3 displays the UV-visible absorption spectra of pyrazoline nanoparticles with different size dispersed in water and the spectrum of pyrazoline dissolved in acetone (1.0×10^{-2} mM). In Figure 3, as the particle size decreases from 130 to 40 nm, $\lambda_{\max}$ of pyrazoline nanoparticles was observed to be shifted the shorter wavelength region by 20 nm. It is

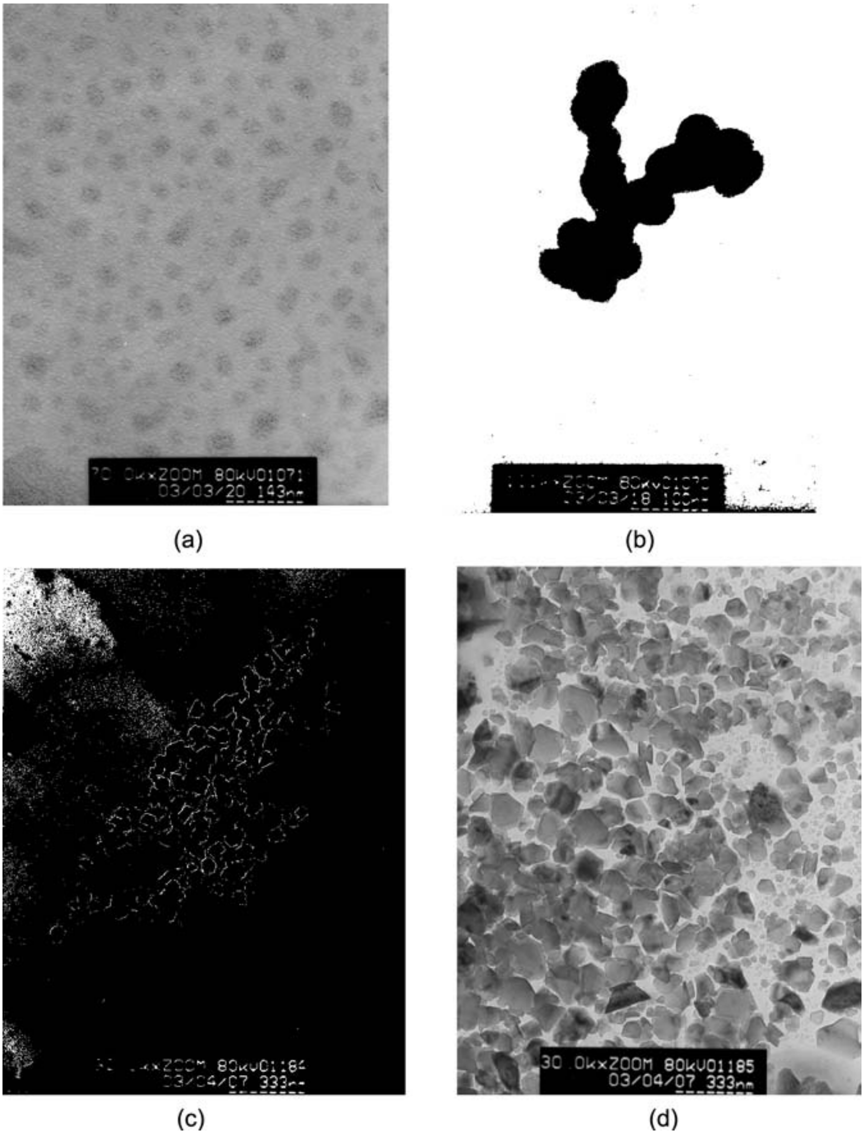

FIGURE 2 The TEM images of pyrazoline nanoparticles with different sizes. (a) 40 nm, (b)65 nm, (c) 90 nm, (d) 130 nm.

interpreted as the more electron delocalization on the main backbone gets $\lambda_{\max}$ to be shifted to a longer wavelength. In Figure 3, we observed that the absorption peak is strongly affected by the nanoparticle sizes. It is expected

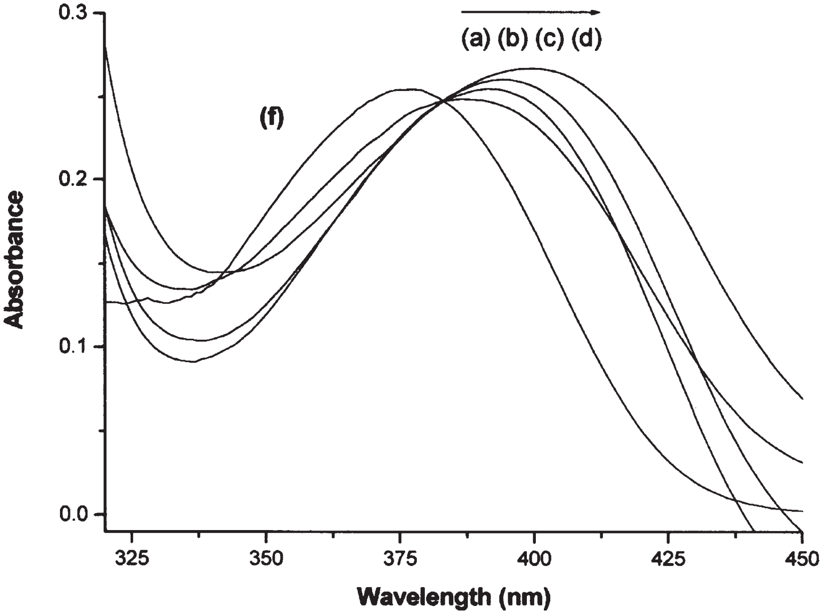

FIGURE 3 The UV-vis absorption spectra of water dispersion of pyrazoline nanoparticles with different sizes; (a) 40 nm; (b) 65 nm; (c) 90 nm, (d) 130 nm, (f) the spectrum of pyrazoline acetone solution (1.0×10^{-2} mM).

for an aggregate state arising from the π–π orbital overlap of closely stacked pyrazoline molecules in nanoparticles and is similar to the previous observations of absorption by aggregate states in other organic molecular crystals such as α-perylene [13] and tetracene [14]. As it is already known by Nakanishi, the reason of size-dependent property is the change of lattice state due to the increase in the surface area. It is likely that the increase in the surface area causes lattice softening, and therefore the Coulombic interaction energies between molecules become smaller, leading to wider band gap.

The fluorescence excitation spectra of pyrazoline nanoparticles with different sizes and pyrazoline monomer in the dilute acetone solution are displayed in Figure 4 and show changes similar to those of the absorption spectra in Figure 3. As the nanoparticle size increases, the peak width becomes broader and the peak also shifts to the longer wavelength region.

Figure 5 displays the fluorescence emission spectra of pyrazoline nanoparticles with different sizes, compared with those of the dilute acetone solution. With increasing nanoparticle size, the peak was shifted to the

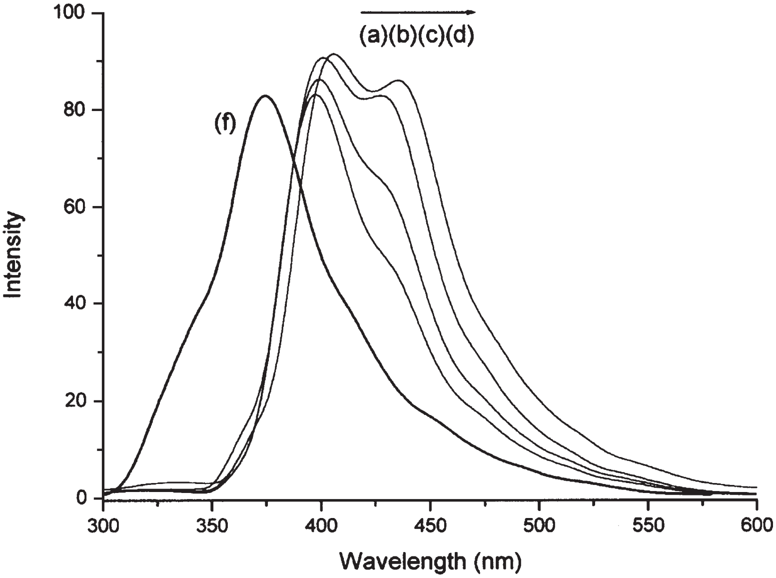

FIGURE 4 The fluorescence excitation spectra of water dispersion of pyrazoline nanoparticles with different sizes; (a) 40 nm; (b) 65 nm; (c) 90 nm, (d) 130 nm, (f) the spectrum of pyrazoline acetone solution (1.0×10^{-2} mM).

longer wavelength region. In Figure 5, the shape of the nanoparticle emission spectrum is similar to that of the dilute solution, and its peak shifts 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 ($v_n = 0, \ldots, n$) of S_1 (labeled $[S_o(0) - S_1(n)]$). Thus, the nanoparticle emission peak is from $S_1(0)$ to $S_o(n)$. The emission spectra indicate that, in nanoparticles, the energy space between $S_1(0)$ and $S_o(n)$ decreases with increasing nanoparticle size because of more rotational and vibrational mode relaxation of non-radiative decay of S_1 state.

As the size of pyrazoline nanoparticle is increased, the red-shift of absorption peak was observed due to molecular aggregation. The grain size of local ordered state may increase as the nanoparticle size increases, allowing the intermolecular electronic interactions to be increased in magnitude and to extend over a larger number of molecules. That is, as the nanoparticle size is increased, the aggregated state gradually forms and the overlap of the pyrazoline rings is gradually enhanced. Therefore, the increase in the intermolecular dipole-dipole interaction leads to narrow band gap, results in the absorption shifting to the lower-energy side. The

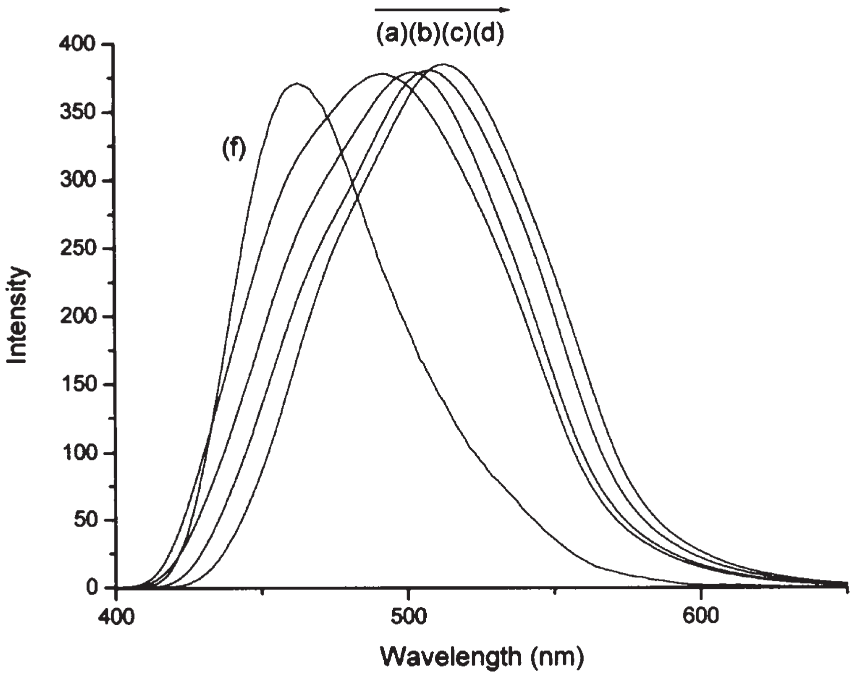

FIGURE 5 The fluorescence emission spectra of water dispersion of pyrazoline nanoparticles with different sizes; (a) 40 nm; (b) 65 nm; (c) 90 nm, (d) 130 nm, (f) the spectrum of pyrazoline acetone solution (1.0×10^{-2} mM).

red-shifted pyrazoline emission peak results from the vibrational characteristics of the excited states with an increase in the particle size. In this study, the size-dependence of absorption and emission exhibited by pyrazoline nanoparticles is due to the aggregate formation and increased intermolecular interaction. The emission color can be modulated by the nanoparticle size.

CONCLUSIONS

1-Phenyl-3-naphthyl-5-((dimethylamino)phenyl)-2-pyrazoline nanoparticles with sizes ranging from tens to hundreds were prepared by the reprecipitation method. We found that the particle size plays a critical role in the 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.

REREFENCES

[1] Micheletto, R., Fukuda, H., & Ohtsu, M. (1995). *Langmuir, 11*, 3333.

[2] Denkov, N. D., Velev, O. D., Kralchevsky, P. A., & Ivanov, I. B. (1993). *Nature, 136*, 26.

[3] Yin, J. S. & Wang, Z. L. (1997). *Phys. Rev. Lett., 79*, 2570.

[4] Bruchez, M., Moronne, M., Gin, P., Weiss, S., & Alivisator, A. P. (1998). *Science, 2013*.

[5] Hagfeldt, A. & Grätzel, M. (1995). *Chem. Rev., 95*, 49.

[6] Schlamp, M. C., Peng, X., & Alivisatos, A. P. J. (1997). *Appl. Phys., 82*, 5837.

[7] Wohltjen, H. & Snow, A. W. (1998). *Anal. Chem., 95*, 49.

[8] Fu, H. & Yao, J. J. (2001). *Am. Chem. Soc., 123*, 1434.

[9] Fu, H., Ji, X., Zhang, X., Wu, S., & Yao, J. J. (1999). *Colloid and Interface Science, 220*, 177.

[10] Fu, H., Xie, R., Wang, Y., & Yao, J. J. (2000). *Colloids and Surfaces A, 174*, 367.

[11] Xiao, D., Xi, L., Yang, W., Fu, H., Shuai, Z., Fang, Y., & Yao, J. J. (2003). *Am. Chem. Soc., 125*, 6740.

[12] Oh, S. W., Zhang, D. R., & Kang, Y. S. (2004). *Mater. Sci. Eng. C, 24*, 131.

[13] Tanaka, J. & Bull. (1963). *Chem. Soc. Jpn., 36*, 1237.

[14] Kelly. M. K., Etchegoin, P., Fuchs, D., Kratschmer, W., & Fostiropoulos, K. (1992). *Phys. Rev. B, 46*, 4963.