

Communication

# Morphology Control over the Organic Nanoparticles of 1,3-Diphenyl-5-(9-anthryl)-2-pyrazoline

XI, Lu<sup>a</sup>(奚璐) XIAO, De-Bao<sup>a</sup>(肖德宝) YANG, Wen-Sheng<sup>a</sup>(杨文胜)  
YAO, Jian-Nian<sup>\*a</sup>(姚建年) ZHANG, Bao-Wen<sup>b</sup>(张宝文)

<sup>a</sup>Key Laboratory of Photochemistry, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

<sup>b</sup>Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101, China

The organic nanoparticles of a blue-light-emitting molecule, 1,3-diphenyl-5-(9-anthryl)-2-pyrazoline, were prepared by reprecipitation method using acetonitrile as the solvent for the molecular precursor. Three morphologies, spherical, doughnut-shaped and cubic, could be observed on the silicon substrate for the nanoparticles by the volume-controlled addition of acetonitrile. The evolution of particle morphology as a function of acetonitrile addition was attributed to the variation of the growth habits of the particles in the different environment. The nanoparticles exhibit the novel photoluminescence spectra as compared to those of monomer and the bulk crystals.

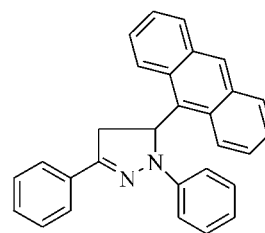
**Keywords** organic nanoparticles, morphology control, reprecipitation method, 1,3-diphenyl-5-(9-anthryl)-2-pyrazoline, photoluminescence

Colloidal systems promise to be of fundamental and technological importance in the development and fabrication of novel optoelectronic devices. Over the last decade, the development of reliable and reproducible methods for producing metal and semiconductor nanocrystallites (quantum dots, rods, tubes and wires)<sup>1-8</sup> with high monodispersity has paved the way for numerous investigations of the quantum confinement effect in inorganic low-dimensional systems. However, study on the nanometer-to-submicron particles prepared from organic molecules is only in its infancy<sup>9</sup> so far, which is relevant to the limited production of colloids from organic nanoparticles. It is reported that the optical properties of organic nanoparticles are also dependent on their size and dimensionality.<sup>9</sup> Thus, the achievement to synthesize high-quality organic colloidal samples with well-controlled sizes and dimensionalities could open up many opportunities for their fundamental research and applications as biological labeling, building blocks in light-emitting diodes, optical non-linear materials or photonic crystals and so on. In light of the fact<sup>9b,10</sup> that pyrazoline derivatives are widely used as brightening agents, hole-conveying medium and light-emitting materials in op-

toelectronic devices, we have successfully prepared a series of spherical organic nanoparticles from a series of pyrazoline derivatives. We observed the size-dependent optical absorption and emission transition<sup>9b</sup> in these organic nanoparticles similar to those in the inorganic ones. However, it is still a challenge to achieve organic nanoparticles with morphology other than sphere.

In this communication, the organic nanoparticles of an alternate pyrazoline derivative, 1,3-diphenyl-5-(9-anthryl)-2-pyrazoline (DAP, Scheme 1) were prepared by reprecipitation method. It was found that the morphologies of DAP nanoparticles could be controlled as spherical, doughnut-shaped or cubic by volume-controlled addition of acetonitrile. The evolution of particle morphology as a function of acetonitrile addition was attributed to the variation of the growth habits of the particles in the different environment.

**Scheme 1** Molecular structure of DAP



The compound DAP was synthesized as described elsewhere,<sup>9b,9c</sup> and purified by liquid chromatography method before use. Acetonitrile (for HPLC use) was used as purchased from ACROS. Ultrapure water with a resistivity of 18.2 MΩ·cm was freshly produced from Millipore-Q Gradient apparatus. The organic colloidal particles of DAP were prepared by the reprecipitation method as previously reported.<sup>9</sup> DAP was insoluble in water but soluble in some organic solvents such as acetonitrile and ethanol. In a typi-

\* E-mail: jnyao@mail.iccas.ac.cn; Fax: 86-10-82616517

Received April 25, 2003; revised July 14, 2003; accepted September 5, 2003.

Project supported by the National Natural Science Foundation of China, Chinese Academy of Sciences and the National Research Fund for Fundamental Key Projects No 973 (No. G19990330).

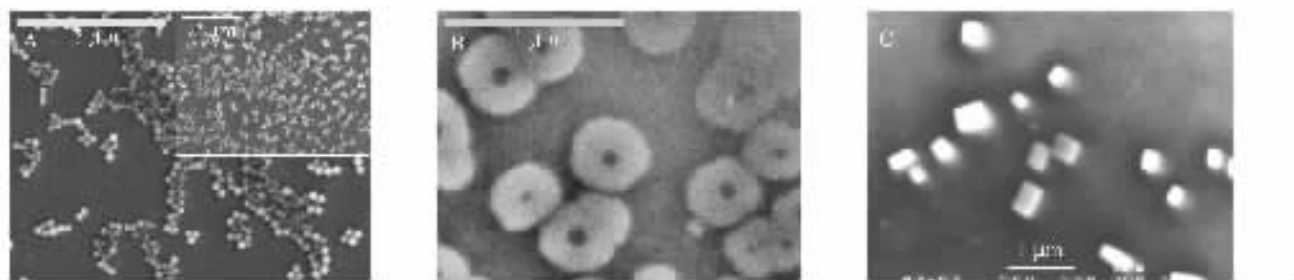
cal synthesis, 200  $\mu\text{L}$  of stock solution ( $1.55 \times 10^{-3}$  mol/L, DAP in acetonitrile) was quickly injected ( $< 2$  s) into 5 mL of ultrapure water using a microsyringe under magnetic stirring at room temperature (*ca.* 25  $^{\circ}\text{C}$ ). The mixing of organic solvent with water phase rapidly changed the character of the system and induced nucleation of DAP particles. The reaction system became turbid during a short period of time after the injection. The growth of DAP particles was carried out at room temperature (25  $^{\circ}\text{C}$ ) for a certain time and the colloidal dispersion was then obtained. The morphology observation of the as-prepared particles by field emission scanning electron microscope (FESEM) was performed on silicon wafer after evaporation of the water.

Several factors possibly influencing the size and morphology of DAP particles were envisaged. While the mixing mode of the DAP solution and water, the aging time, and the temperature at which the suspension was aged determined the average particle size and the size distribution of the particles, these three factors showed little effect on the morphology of the particles. In our research, when 200  $\mu\text{L}$  of DAP stock solution ( $1.55 \times 10^{-3}$  mol/L) was injected into 5 mL of water, and was aged for 10 h at 25  $^{\circ}\text{C}$ , all the DAP particles obtained were observed to be spherical, as shown in the FESEM image in Fig. 1A. The change of the above-mentioned factors allowed us only to prepare the spherical particles with different average size and the size distribution, similar to those observed in the preparation of nanoparticles from other pyrazoline derivatives.<sup>9b, 9d</sup> For example, under the same condition as above-mentioned, the spherical particles with larger average diameters (300 nm) were obtained after the samples were aged for 15 h. The particles with the mean diameter of 120 nm can be prepared when 150  $\mu\text{L}$  of DAP stock solution ( $1.55 \times 10^{-3}$  mol/L) was injected into 5 mL of water at room temperature and then was placed onto silicon after aged for 4 h at 25  $^{\circ}\text{C}$  (Inset of Fig. 1A). However, the morphology of the

particles can be influenced greatly by the addition volume of acetonitrile in the suspension system. For example, the doughnut-shaped particles were observed when 200  $\mu\text{L}$  of DAP stock solution ( $1.55 \times 10^{-3}$  mol/L) was injected into a mixture of 5.00 mL of water and 0.10 mL of acetonitrile (Fig. 1B), and was aged for 10 h at 25  $^{\circ}\text{C}$ . The particles were observed as cubic (Fig. 1C) when the same 200  $\mu\text{L}$  of DAP stock solution ( $1.55 \times 10^{-3}$  mol/L) was injected into a mixture of 5.00 mL of water and 0.30 mL of acetonitrile under the same condition of aging time and aging temperature. The cubic particles possess the average particle size of 350 nm and the average aspect ratio of 1.5. It is noted that the solvent in all the samples was removed under the same relative humidity of 40% at 25  $^{\circ}\text{C}$ . From these experimental results it is suggested that the morphology of the particles evolves as a function of the volume of acetonitrile in the dispersions.

The selected area electron diffractions (SAED) on transmission electron microscope (JEOL JEM-200CX) show that the as-prepared spherical particles as shown in Fig. 1A is amorphous, the crystallinity degree of the doughnut-shaped particles in Fig. 1B has been increased compared with spherical ones, and the cubic particles in Fig. 1C are polycrystalline. XRD (D/max-2400 X-Ray Diffractometer with an X-ray source of Cu/K $\alpha$  at 40 kV and 120 mA) confirms that the spherical particles are amorphous, however, the crystallinity of the latter two particles was not characterized by XRD because of their small quantity. The surface electric determination of the spherical DAP particles indicated that they are negatively charged and the  $\xi$ -potentials for the different-sized particles kept at the same value of about -30 mV.

It is known that the crystallization process includes two stages: nucleation and crystal growth.<sup>11</sup> The crystalline morphology is determined by the relative growth rates of the different crystallographic planes. The growth kinetics is greatly influenced by internal factors as the crystal stru-

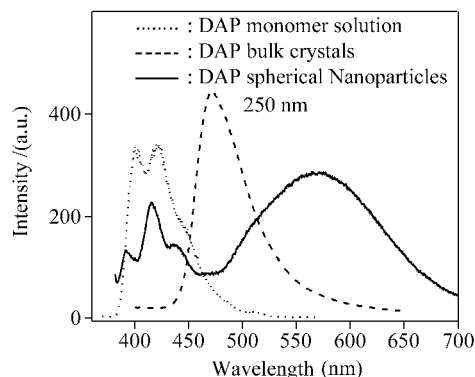


**Fig. 1** FESEM images of DAP colloidal particles on silicon substrate. (A) 250 nm of spherical particles, 200  $\mu\text{L}$  of DAP stock solution ( $1.55 \times 10^{-3}$  mol/L) was injected into 5 mL of water at room temperature and then was placed onto silicon after aged for 10 h at 25  $^{\circ}\text{C}$ . Inset of (A): 120 nm of particles, 150  $\mu\text{L}$  of DAP stock solution ( $1.55 \times 10^{-3}$  mol/L) was injected into 5 mL of water at room temperature and then was placed onto silicon after aged for 4 h at 25  $^{\circ}\text{C}$ . (B) 400 nm of doughnut-shaped particles, 200  $\mu\text{L}$  of DAP stock solution ( $1.55 \times 10^{-3}$  mol/L) was injected into the mixture of 5 mL of water and 0.1 mL of acetonitrile at room temperature and then was placed onto silicon after aged for 10 h at 25  $^{\circ}\text{C}$ . (C) 350 nm of cubic particles, 200  $\mu\text{L}$  of DAP stock solution ( $1.55 \times 10^{-3}$  mol/L) was injected into the mixture of 5 mL of water and 0.3 mL of acetonitrile at room temperature and then was placed onto silicon after aged for 10 h at 25  $^{\circ}\text{C}$ . The solvent in all the three samples was removed under the relative humidity of 40% at 25  $^{\circ}\text{C}$ . The scale bar in inset of (A) and in (C) are 2 and 1 micrometer, respectively.

cture, and external factors as solvents, supersaturation, and hydrodynamic properties. These factors are determined to be the same in the three systems except for the amount of acetonitrile. The change in the amount of acetonitrile may affect the evolution of the particle morphology in two ways. On one hand, the change of the acetonitrile volume varied the supersaturation. On the other hand, it also changed the polarity of the system. For the crystals precipitated from solution, the choice of solvent influences the crystal habit.<sup>12</sup> It is well known that the growth habits of polar organic crystals depend strongly on the polarity of solvents from which they are grown, because growth units with different structures form in different solvents.<sup>13</sup> DAP is a kind of polar organic molecule. The different growth units may potentially form in the mixtures with different percentage of the components, which eventually leads to the different growth rate of the planes. Thus, the particles with different morphologies are prepared in different media. Furthermore, the amorphous structure of the spherical particles in Fig. 1A may be the result of the large supersaturation due to the small amount of the good solvent, acetonitrile presented.

It should also be noted that the size of DAP nanoparticles were influenced by the addition of acetonitrile. For instance, as shown in Fig. 1, the size of the particles with different shapes were 250, 400 and 350 nm, respectively. It is believed that the evolution of the particle size as a function of addition of acetonitrile may be related to the change of supersaturation in different systems, which also lead to the difference in quantity of nuclei in the period of nucleation, and the growth rate of the particles.

Fig. 2 displays the photoluminescence spectra of the spherical particles, monomers and the bulkcrystals. The absence of characteristic of pyrazoline chromophore in monomer system is induced by the solvent quenching. However, the bulk crystals exhibit the only feature of pyrazoline moiety. It is worthy to the spherical particles present the emission of anthracene moiety, and a new broad and structureless peak at 570 nm, which is potentially attributed to anthracene excimer.<sup>14</sup> The formation of the excimer



**Fig. 2** Photoluminescence spectra of DAP spherical nanoparticles, monomers and the bulk crystals. The excitation wavelength is at 365 nm.

may be related to the preferential stacking mode in the nanoparticles.<sup>9d</sup> This indicated that the as-prepared DAP nanoparticles exhibit the novel optical performance, which differ distinctively from the monomer and the bulk crystals.

In summary, we observed the organic colloidal particles of DAP with different shapes on silicon substrate. The control of addition of acetonitrile can be used to vary the shapes and the sizes of the resulting DAP particles from spherical morphology to cubic one, which is attributed to the different growth habits induced by the different supersaturation and polarity in the growth environment. The nanoparticles exhibit the novel photoluminescence spectra as compared to those of monomer and the bulk crystals. The work demonstrates a possibility to exert control over the morphology for the organic colloidal particles. The achievement to the synthesis of particles with different shapes from small organic semiconductor molecules in a large scale may present novel candidates of materials for the fundamental and application research of electroluminescence and photonic crystals. The further investigations regarding the large-scale preparation of the shape-controlled organic nanoparticles are now underway.

## References

- Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.
- Micic, O. I.; Sprague, J. R.; Curtis, C. J.; Jones, K. M.; Machol, J. L.; Nozik, A. J.; Gie, H.; Mssen, K.; Fluegel, B.; Mohs, G.; Peyghambarian, N. *J. Phys. Chem.* **1995**, *99*, 7754.
- Alivisatos, A. P.; Harris, A. L.; Levinos, N. J.; Steigerwald, M. L.; Brus, L. E. *J. Chem. Phys.* **1988**, *89*, 3435.
- Norris, D. J.; Bawendi, M. G. *Phys. Rev. B* **1996**, *53*, 16338.
- Nirmal, M.; Murray, C. B.; Bawendi, M. G. *Phys. Rev. B* **1994**, *50*, 2293.
- Temer, S. A.; Wang, Z. L.; Travis, C. G.; Armin, H.; Mostafa, A. E. *Science* **1996**, *272*, 1924.
- Peng, Z. A.; Peng, X. G. *J. Am. Chem. Soc.* **2001**, *123*, 1389.
- Victor, F. P.; Kannan, M. K.; Alivisatos, A. P. *Science* **2001**, *291*, 2115.
- (a) Kasai, H.; Kamatani, H.; Okada, S.; Oikawa, H.; Matsuda, H.; Nakanishi, H. *Jpn. J. Appl. Phys.* **1996**, *35*(2B), L221.  
(b) Fu, H. B.; Yao, J. N. *J. Am. Chem. Soc.* **2001**, *123*, 1434.  
(c) Xiao, D. B.; Tian, Z. Y.; Xi, L.; Zhao, L. Y.; Yang, W. S.; Yao, J. N. *Chin. J. Chem.* **2003**, *21*, 79.  
(d) Fu, H. B.; Loo, B. H.; Xiao, D. B.; Xie, R. M.; Ji, X. H.; Yao, J. N.; Zhang, B. W.; Zhang, L. Q.; *Angew. Chem., Int. Ed.* **2002**, *41*, 962.

- 10 Sandler, S. R.; Tsou, K. C. *J. Chem. Phys.* **1963**, *39*, 106.
- 11 Mullin, J. W. *Crystallization*, 3rd ed., Butterworth Heine-  
mann, Oxford, **1993**.
- 12 Remika, P. J. *J. Am. Chem. Soc.* **1954**, *76*, 940.
- 13 (a) Wang, B. G.; Shi, E. W.; Zhang, W. Z. *Acta Chim. Sinica* **1998**, *56*, 320 (in Chinese).  
(b) Wang, B. G.; Shi, E. W.; Zhang, W. Z.; Yin, Z. W. *Acta Chim. Sinica* **1997**, *55*, 430 (in Chinese).
- 14 Chandross, E. A.; Ferguson, J.; McRae, E. G. *J. Chem. Phys.* **1966**, *45*, 3546.

(E0304254 LI, L. T.; LU, Z. S.)