The Size-dependent Property of 1,3,5-Triphenyl-2-pyrazoline Microcrystals
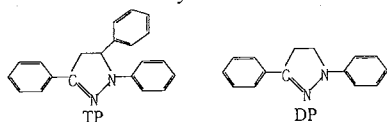
Hong-Bing Fu, Xue-Hai Ji, and Jian-Nian Yao*

Institute of Photographic Chemistry, CAS, Beijing 100101, P.R. China

1,3,5-Triphenyl-2-pyrazoline microcrystals with different sizes from 300 nm to 30 nm were prepared by the reprecipitation method and their absorption peak was found to shift to higher energy side with decreasing crystal size due to size effect and J-aggregate effect.

In the recent decades, nanoparticles of semiconductors and metals have stimulated much interest due to their unusual mesoscopic properties.[1] At present, studies of organic nanoparticles are increasing, but most of which focus on polymers.[2] Preparation of nanoparticles of general organic molecules has been scarcely reported. Nakanishi prepared microcrystals of perylene and polydiacetylene by the simple reprecipitation method and found that the polydiacetylene microcrystals was a new type of material in third order non-linear optics.[3-4] 2-Pyrazolines possess a large molecular hyperpolarizability. The two-dimensional array constructed with their nanoparticles is a new type of photofractive materials.[5] In this present work, we prepared pyrazoline microcrystals ranging from tens to hundreds nanometers using the above-mentioned reprecipitation method and studied their optical size-dependent property, which are different from the isolated molecules and bulk crystals.

1,3,5-Triphenyl-2-pyrazoline (TP) and 1,3-diphenyl-2-pyrazoline (DP) were gifts from professor S. K. Wu (Institute of Photographic Chemistry, CAS) and were used without further purification. Microcrystals of TP were prepared by the reprecipitation method[3-4] as follows: 200 μl of TP/acetone solution (7.5×10^{-4} mol·L^{-1}) was injected into 10 ml of water with vigorous stirring, using a 100 μl microsyringe. By controlling the quantity of TP/acetone solution and the aging time, the size of microcrystals could be controlled. For example, when 50 μl and 200 μl of TP/acetone solutions were injected, the crystal sizes prepared finally were 80 nm and 300 nm, respectively.

We successfully prepared TP microcrystals with different sizes from tens to hundreds nanometers. Some of their TEM photographs were shown as Figure 1, in which the crystal sizes were 30 nm and 80 nm. It can be seen from Figure 1 that, as the size of TP microcrystals decreased, the tendency to uniform size distribution was enhanced and the shape of TP microcrystals changed from cubic to amorphous. Figure 2 displays the UV-visible absorption spectra of TP microcrystals dispersed into water with different sizes and the spectrum of TP/acetone solution (1.5×10^{-6} mol·L^{-1}). Apparently, going from spectrum (d) to spectrum (a) with decreasing crystal size, the

width of absorption peak became narrower and its shape changed from asymmetric to symmetric, and at the same time, the absorption peak of TP microcrystals was observed to shift to shorter wavelength region. This size-dependence of TP microcrystals is different from TP monomer and bulk crystals.[6] In addition, the spectra of DP in acetone (1.0×10^{-6} mol·L^{-1}) and its microcrystals dispersion into water were measured. The diffuse reflectance spectrum of DP bulk crystals was also measured. The absorption peaks were all observed at about 350 nm and their shapes were symmetric. That is to say, DP microcrystals do not possess the optical size-dependent property. This difference between TP microcrystals and DP microcrystals possibly results from the difference of molecular structure between TP and DP, as will be discussed below.

The absorption for the crystal size of 300 nm (Figure 2(d)) is asymmetric and actually consists of two peaks. One is at 408 nm, which is attributed to absorption of aggregate; and the other is at shorter wavelength, which is attributed to molecular absorption peak.[7] According to the theory of aggregates, when the stacking angle that defines the angle between the transition dipole and the molecular axis of aggregate is 54°44' or less, the absorption peak of aggregate is red-shifted from that of
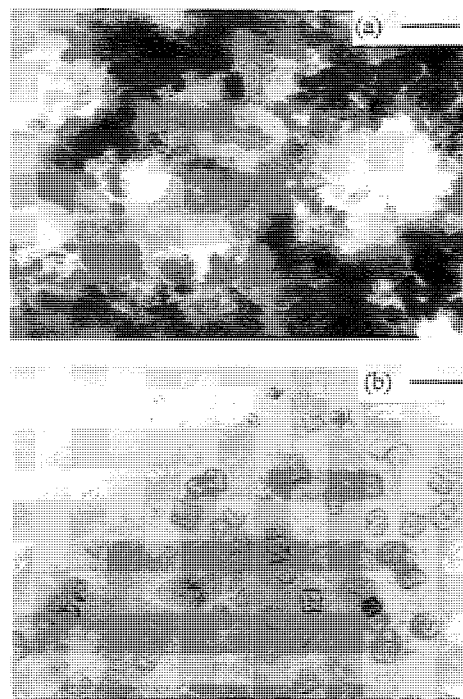
1,3,5-Triphenyl-2-pyrazoline (TP) and 1,3-diphenyl-2-pyrazoline (DP)

TP

DP

Figure 1. TEM photographs of TP microcrystals with different sizes, (a) 30 nm, (b) 80 nm. The length of horizontal bar is 200 nm.
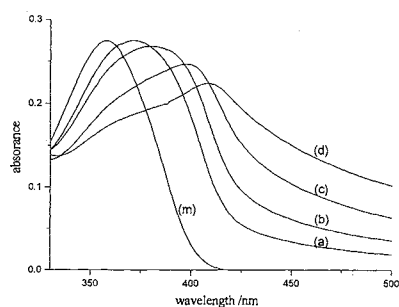
Figure 2. UV-visible absorption spectra of water dispersion of TP microcrystals with different sizes: (a) 30 nm, (b) 80 nm, (c) 200 nm, (d) 300 nm. (m) spectrum of TP/acetone solution (1.5×10^{-6} mol·L⁻¹).

Table 1. The results of two-peaks-fitting to the spectra of TP microcrystals with different sizes

Spe-ctra	Size	Maximum wavelength[a]	Peak 1[b]		Peak 2[b]	
			Posi-tion	Percen-tage[c]	Posi-tion	Percen-tage[c]
/nm		/nm	/nm	/%	/nm	/%
m	/	358	358	100	/	/
a	30	370.8	373	99.7	406	0.3
b	80	379.2	378.7	94.1	407.4	3.9
c	200	396.2	384	89	407	11
d	300	408	391	84	410	16

[a] Directly obtained from the software of Shimadzu UV-1601 PC. [b] Obtained from the two-peaks-fitting using Lorents. [c] referring the area sum of peak 1 + peak 2 as 100% in every spectrum.

monomer and is attributed to J-aggregate.[8] Compared with the monomer absorption peak at 358 nm (Figure 2(m)), the absorption peak of aggregate is red-shifted to 408 nm. Moreover, in our experiments, the appearance of aggregate absorption upon going from spectrum (a) to spectrum (d) is similar to the spectra change of the J-aggregate growth in thiacarbocyanine LB film.[9] Therefore, the peak which is at 408 nm in Figure 2(d) can be attributed to J-aggregate absorption. In order to probe the detailed change of the spectra of TP microcrystals with different sizes, we carried out a two-peaks-fitting of the spectra shown in Figure 2, using Lorentzian functions. Table 1 displays the results of the fitting, in which peak 1 represents the molecular absorption peak and peak 2 represents the J-aggregate absorption peak.

According to Table 1, as the TP microcrystal size decreased from 300 nm to 30 nm, the molecular absorption peak blue shifted from 391 nm to 373 nm and the percentage of its area increased from 84.0% to 99.7%. On the other hand, the area of J-aggregate absorption peak gradually decreased from 16% to 0.3%. These results suggest that two aspects could be taken into consideration of the optical size-dependence of TP microcrystals. First, it is the disappearance of J-aggregate absorption peak. Owing to the decreasing of crystal size, the quantity of molecules in a single microcrystal decreases, and therefore, the tendency to form J-aggregate weakens. The second is the blue-shift of molecular absorption peak. The first mainly influences the shape of spectra of microcrystals due to the small percentage of J-aggregate absorption and the second mainly leads to the blue-shift of spectra of microcrystals with decreasing crystal size.

This optical size-dependent property of TP microcrystals differs from the so-called "quantum confinement effect".[1] To explain the same size-dependence of perylene microcrystals as

that in our experimental results, Nakanishi considered two reasons for it.[3] One is the change of lattice-state due to the increase in surface area as a result of microcrystallization. It is likely that microcrystallization causes lattice softening, and therefore the Coulombic interaction energies between molecules become smaller, leading to wider band gaps. The other reason may be the electric field effect of surrounding media through the surface of microcrystals. Summing up Nakanishi's explanation and the molecular structure of TP, the detailed reason for the blue-shift of the molecular absorption peak of TP microcrystals is considered to be as follows. In the TP molecule, the angle between 1-position and 5-position phenyl rings is statistically random to some extent. So the dipole-dipole interaction energies are small, leading to wide band gaps. In bulk crystals, the angle is a certain value due to the bondage of lattice. Thus the dipole-dipole interaction energies are larger, leading to narrower band gaps. In microcrystals, as the proportion of surface molecule increases as a result of crystal size decreasing, the statistical uncertainty of the angle is developing. Therefore, the dipole-dipole interaction energies in microcrystals gradually decreases upon going from the TP bulk crystals to TP molecule, and leading to gradually widening of band gaps. Considering two molecular structures of TP and DP, it seems that TP who possesses the phenyl ring at 5-position shows the optical size-dependence. In 2-pyrazolines, the charge distribution of N-1 (N at 1-posotion) changes from negative in the ground state to positive in the excited state because of the conjugated charge-transfer from N-1 to C-3.[5] TP possessing the phenyl ring at 5-position results in the non-conjugated charge-transfer from C-5 to N-1[5] and the changes of the dipole-dipole interaction energy in these three cases. As for DP, the angle between the phenyl planes at 1-position and 3-position is fixed at 11° and the phenyl at 5-position does not exist.[10] So the dipole-dipole interaction energy of DP in these three cases is approximately the same, leading to stable band gaps, and therefore the absorption peaks are all at about 350 nm. It shows that the above explanation for the blue shift of the molecular absorption peak of TP microcrystals is reasonable. That is to say, besides the influence of J-aggregate, the size effect and the surface effect cause this optical size-dependence of TP microcrystals.

References and Notes

1 E. Hanamura, *Phys. Rev. B*, **37**, 1273 (1988).
2 R. Micheletto, H. Fukuda, and M. Ohtsu, *Langmuir*, **11**, 3333 (1995).
3 H. Kasai, H. Kamatani, S. Okada, H. Oikawa, H. Matsuda, and H. Nakanishi, *Jpn. J. Appl. Phys.*, **35**, 221 (1996).
4 H. Katagi, H. Kasai, S. Okada, H. Oikawa, H. Matsuda, and H. Nakanishi, *J.Macromol.Sci., Pure. Appl. Chem.*, **A34(10)**, 2013 (1997).
5 J. O. Morley, *J. Mol. Electronics*, **5**, 117 (1989).
6 The diffuse reflectance spectra of TP bulk crystals shows a broad absorptive band from 480 nm to 200 nm.
7 S. R. Sandler and K. C. Tsou, *J. Chem. Phys.*, **39**, 1062 (1963).
8 E. S. Emerson, M. A. Conlin, A. E. Rosenoff, K. S. Norland, and H. Rodriguez, D. Chin, G. R. Bird, *J. Phys. Chem.*, **71**, 2396 (1967).
9 M. H. Liu, A. Kira, and H. Nakahara, *J. Phys. Chem.*, **100**, 20138 (1996).
10 B. Duffin, *Acta Cryst*, **B24**, 1256 (1968).