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# Characterization of the size-dependent optical properties of *p*-terphenyl nanocrystals

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**Abstract**

*p*-Terphenyl (TP) nanocrystals with different sizes from 50 to 300 nm were prepared by the reprecipitation method. Their main absorption peaks attributed to $^1L_a \leftarrow {}^1A$ transition were observed to shift to longer wavelength region with increasing crystal size. At the same time, a new peak assigned to $^1L_b \leftarrow {}^1A$ absorption emerged and became stronger. This size-dependent property of the absorption spectra may be attributed to the interaction between TP molecules. The fluorescence excitation spectra of TP nanocrystals also exhibited size-dependent properties, as well as absorption spectra, and the difference between the emission spectra of TP monomer and those of TP nanocrystals may result from different configuration of the TP molecules in the two states. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* *p*-Terphenyl nanocrystals; Size-dependent property

## 1. Introduction

In recent years, quantum dots have attracted much more attentions due to their size-dependent optical and electrical properties. Studies on quantum dots are devoted to the understanding of fundamental physicochemical properties of materials as a function of size, from isolated atom or molecule to bulk crystal [1]. Quantum dots can be integrated into complex assemblies, which will bring about many opportunities for scientific discovery. The construction of quantum dots into optical and electrical devices has just started. Current research in the quantum dots is mainly focused on nanocrystals or clusters of metal and semiconductor, because of the strong interaction between nearest atoms. While considering organics, Forrest has reported multiple quantum well structure grown by organic molecular beam deposition (OMBD) [2], but the research on organic nanocrystals was scarcely undertaken. Nakanishi and co-workers have carried out some initial works in this field [3–5]. They prepared aqueous dispersions of nanocrystals of perylene, diacetylene through reprecipitation method, a versatile and simple process to fabricate organic nanocrystals. In these dispersions, some interesting phenomena, such as the variations of the linear and non-linear optical properties with nanocrystal sizes, have been observed. They also constructed electrostatic self-assembly films of polydiacetylene nanocrystals, which allow the prospective application of organic nanocrystals as novel optical materials [6].

*p*-Terphenyl (TP) is well known as an organic scintillator. It has a very intensive absorption band and high quantum yield, which make it possible to realize blue light-emitting organic electroluminescent (EL) devices [7]. In the present study, we prepared TP nanocrystals in the range of crystal size from tens to hundreds nanometers using the above-mentioned reprecipitation method, and evaluated their size-dependent optical properties in absorption and fluorescence spectra, which were different from those of the isolated molecule and bulk crystals.

## 2. Experimental details

### 2.1. Materials

The compound TP was purchased from Acros Company and used without further purification. Nanocrystals of TP were prepared as follows: 400 μl of TP/ethanol solution ($9.70 \times 10^{-4}$ mol l$^{-1}$) was injected into 10 ml of water. After vigorous stirring, white dispersion was formed. By controlling the aging time and the amount of the added TP solution, the crystal size could be controlled. For example, when 200 and 400 μl TP/ethanol solutions were injected, the sizes of nanocrystals finally prepared were 200 and 300 nm, respectively. The samples for an X-ray diffraction (XRD) test are collected on membrane filters (Anodisc 13, Whatman,

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diameter of the pore is 20 nm) after filtration. The water used in this experiment was purified by a Milli-Q plus water purification system and had a resistivity of 18.2 MΩ.

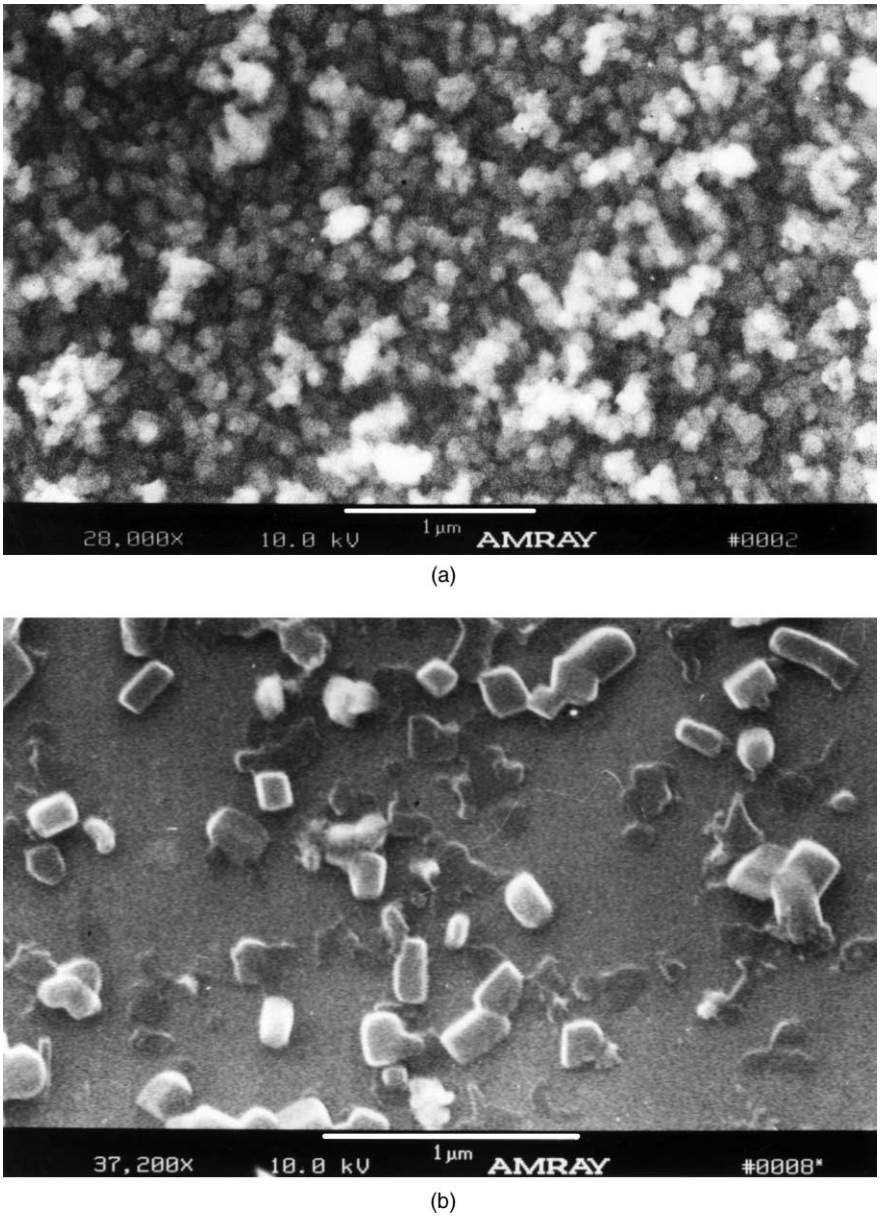
### 2.2. Methods

The UV–VIS absorption spectra of TP nanocrystals dispersed in water were measured using Shimadzu UV-1601 PC double beam spectrophotometer. The fluorescence spectra were recorded by F-4500 Hitachi fluorescence spectrophotometer. The size and shape of the nanocrystals were observed by using a AMARY field emission scanning electron microscopy (AMARY 1910FE). The size, its distribution, and $\xi$-potential of the nanocrystals dispersed in water were also investigated by the dynamic light-scattering (DLS) technique using a Zetplus BI-9000 (Brookhaven Instruments Corp., USA). XRD was carried out with Rigaku D/max-2500 XRD instrument with a X-ray source of Cu K$\alpha_1$ radiation ($\lambda = 0.154056$ nm) calibrated by a slit and monochromized by graphite.

## 3. Results and discussion

### 3.1. SEM image of TP nanocrystals

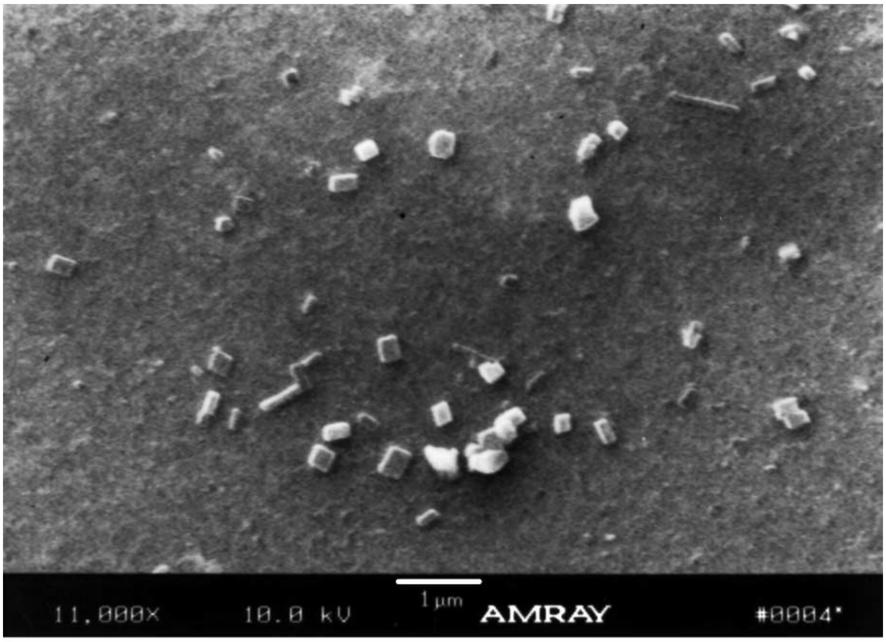
A series of TP nanocrystals from several tens to hundreds nanometers in size were prepared in this experiment. Some SEM photographs of the nanoparticles were displayed in Fig. 1, in which the average crystal sizes were 80, 200 and



(a)

(b)

Fig. 1. The SEM photographs of TP nanocrystals with different sizes: (a) 80 nm, (b) 200 nm, (c) 300 nm



(c)

Fig. 1. (*Continued*).

300 nm, respectively. These values agree roughly with those determined by DLS. It can be seen from Fig. 1, that as the size increased, the shape of TP nanocrystals changed from sphere to cubic with sharp and distinct edges. The small spherical particles, as shown in Fig. 1a, were confirmed to be crystallization as indicated by XRD measurement. Its XRD pattern shows peaks at the same positions as those of TP bulk crystal (Fig. 2b). However, the S/N ratio of the XRD pattern peaks was much low, owing to the broad peak of amorphous halo from the membrane filter. When the sizes increase, the XRD patterns of the nanocrystals also show peaks at the same position but narrow half-height peak widths. The SEM photographs also showed that the distribution of crystal size became broader with increasing crystal size as confirmed by DLS. The $\xi$-potential measured was about $-25$ mV, being independent of crystal sizes.

### 3.2. Absorption spectra of TP nanocrystals

Fig. 3 displays the UV–VIS absorption spectra of TP nanocrystals with different sizes dispersed in water and the absorption spectrum of TP/ethanol solution (dashed line).

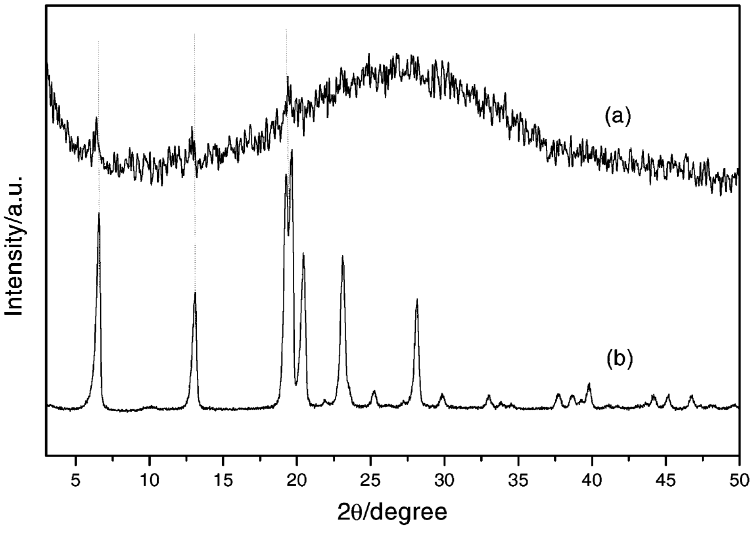


Fig. 2. (a) XRD patterns of TP nanocrystals (80 nm) and (b) XRD patterns of TP bulk crystals. In (a), the background or the wide peak is owing to the amorphous structure of membrane filters.

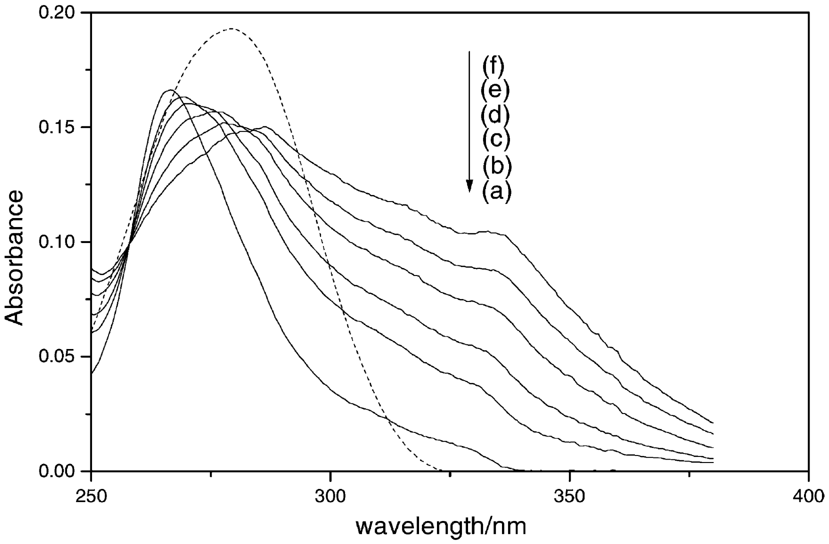


Fig. 3. UV–VIS absorption spectra of TP nanocrystals dispersed in water with different sizes: (a) 50 nm, (b) 80 nm, (c) 150 nm, (d) 200 nm, (e) 250 nm, (f) 300 nm. Dashed line: the absorption spectrum of TP/ethanol solution ($3.9 \times 10^{-5}$ mol l$^{-1}$).

These spectra have a main maximum in the wavelength between 250 and 300 nm, which is attributed to $\pi^* \leftarrow \pi$ transition parallel to the longest molecular axis and is generally denoted as $^1L_a \leftarrow {}^1A$ transition. From Fig. 3, it can be seen from spectrums a–f with increasing crystal size, these absorption peaks of TP nanocrystals shifted to longer wavelength region along with broadening of the peak width. It can also be found from Fig. 3, that a new peak emerged around 330 nm when crystal size increased. To clarify the detailed change of this new absorption peak, the background of conjugation band and tailing edge caused by scattering effect was subtracted as reported by Uchida et al. [8]. The result is displayed in Fig. 4. Although this method may lead to somewhat errors, depending on the way to subtract the strong background, it is possible to investigate not the exact positions, but the tendency of spectra changes within experiment error. Similar to the absorption in TP bulk crystals and LB film [8–11], this weak absorption band along with its small shoulder peak should be assigned to the $^1L_b \leftarrow {}^1A$ transition perpendicular to the longest molecular axis, which can be correlated with organization or association of TP molecules.

The changes of $^1L_a \leftarrow {}^1A$ and $^1L_b \leftarrow {}^1A$ transition were summarized in Table 1. As shown in Table 1, when crystal size increased from 50 to 300 nm, the absorption peaks of $^1L_a \leftarrow {}^1A$ transition shifted from 266 to 286 nm. At the

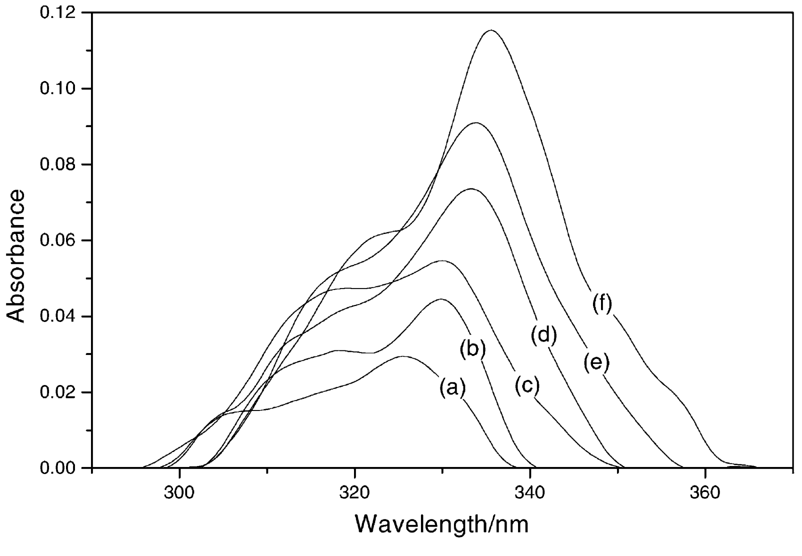


Fig. 4. The spectra of weak absorption, obtained by subtracting strong background absorption of spectra in Fig. 2, with different TP nanocrystal sizes: (a) 50 nm, (b) 80 nm, (c) 150 nm, (d) 200 nm, (e) 250 nm, (f) 300 nm.

Table 1
Positions and absorbance of the two absorption peaks of TP nanocrystals

| Spectrum | Nanocrystal size (nm) | Peak position of $^1L_a \leftarrow {}^1A$ transition[a] (nm) | Absorbance of $^1L_a \leftarrow {}^1A$ transition | Peak position of $^1L_b \leftarrow {}^1A$ transition[b] (nm) | Absorbance of $^1L_b \leftarrow {}^1A$ transition |
|---|---|---|---|---|---|
| Monomer | – | 278.8 | – | – | – |
| a | 50 | 266.0 | 0.166 | 325.4 | 0.029 |
| b | 80 | 269.0 | 0.164 | 329.8 | 0.045 |
| c | 150 | 270.5 | 0.160 | 330.3 | 0.055 |
| d | 200 | 275.5 | 0.157 | 333.2 | 0.074 |
| e | 250 | 280.0 | 0.153 | 333.7 | 0.091 |
| f | 300 | 285.6 | 0.149 | 335.6 | 0.115 |

[a] Directly obtained using the software of Shimadzu UV-1601 PC.
[b] Obtained from Fig. 3 (the position and absorbance of this peak cannot be directly obtained using the software of Shimadzu UV-1601 PC).

mean time, the absorption peaks of $^1L_b \leftarrow {}^1A$ transition shifted from 325 to 335 nm, accompanied with the increase in absorbance. These spectra are entirely different from absorption of TP monomers (dashed line) and TP bulk crystals reported in previous work [12], and a size-dependent optical property should be taken into consideration. This size-dependent property is different from so-called 'quantum size effect', because the quantum size effect is observed in semiconductors fine particles whose size is <10 nm. Also, it is unlikely to be due to Mie scattering, which is often observed in metal particles. Actually, Mie scattering can affect the peak position of absorption spectra, however, it cannot explain the change of peak width of the spectra in Fig. 3 [5]. Nakanishi and co-workers suggested two reasons for this kind of phenomenon. One is the change of lattice state due to the decrease in surface area as a result of increased crystal size, and the other is the electric field effect of surrounding media on the surface of the nanocrystals [5]. Since the $\xi$-potential of the aqueous suspension had no significant changes regardless of crystal sizes in our experiment, the electric field may not be, at least, the principal factor.

Based on the above discussions, a schematic representation of the transitions of the TP molecules in solution and nanocrystals can be illustrated as shown in Fig. 5. In ethanol solution, the isolated TP molecules are free-standing and randomly dispersed, thus, the interaction between those molecules is pretty weak, leading to wider band gaps. At this state, the $^1L_b \leftarrow {}^1A$ transition parallel to short molecular is weak, which is hidden by the strong $^1L_a \leftarrow {}^1A$ transition. In bulk crystals, TP molecules are essentially planar [8], and the molecules are tightly constrained by the lattice. Thus, the interaction energies are larger, resulting in narrower band gaps. In smaller nanocrystals, TP molecules precipitated from the solution may initially aggregate with each other as TP molecules in LB film [11] and H-aggregates in β-carotene nanoparticles [13], but are not highly restrained at the lattice site due to the soft lattice. At this stage, the $^1L_b \leftarrow {}^1A$ transition emerges, resulting from the strong interaction between overlaid molecules, which induces the short axis polarized transition. As the size of the TP nanocrystals increases, the fraction of molecules on the surface decreases and the crystal lattice become tightened. Hence, the van der Waals interaction or transition dipole–dipole interaction between TP molecules becomes stronger. Consequently, the energy gap becomes narrower and narrower gradually. As a result, the absorption peaks of $^1L_b \leftarrow {}^1A$ and $^1L_a \leftarrow {}^1A$ transition shift to lower energy side. Also, the intensity of $^1L_b \leftarrow {}^1A$ absorption, short axis transition, was enhanced in this process, because more molecules are highly overlaid. Many researches have proven the change of the geometry of molecule might induce the shift of absorption spectra. For example, TP molecule is proved to be twisted in solution and be planar in crystals [14], thus, when dihedral angle of TP molecule decreases in the process of crystal formation, the absorption peak may experience red-shift to some extent.

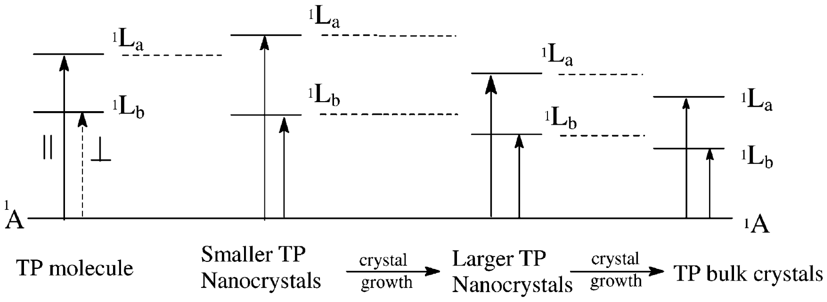


Fig. 5. Schematic illustration of the change of transition energy of TP nanocrystals in the process of crystal growth. The || and ⊥ lines denote the polarization directions of transitions parallel and perpendicular to the longest molecular axis, respectively.

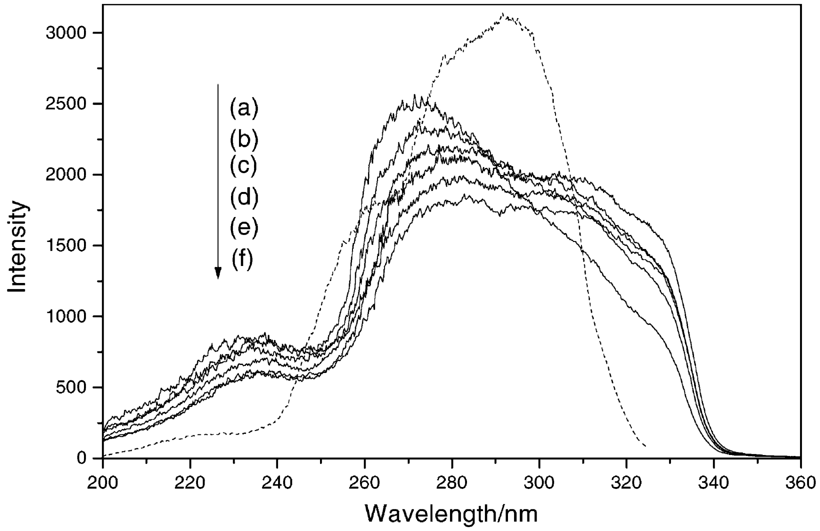


Fig. 6. Fluorescence excitation spectra of TP nanocrystals dispersed in water with different sizes: (a) 50 nm, (b) 80 nm, (c) 150 nm, (d) 200 nm, (e) 250 nm, (f) 300 nm. Dashed line: the excitation spectrum of TP/ethanol solution ($3.9 \times 10^{-5}$ mol l$^{-1}$).

### 3.3. Fluorescence spectra of TP nanocrystals

Fig. 6 illustrates the fluorescence excitation spectra of TP nanocrystals. In Fig. 6, the changes of the excitation spectra were consistent with the absorption spectra. With increasing crystal size, the main peak around 280 nm shifted to longer wavelength, which can be assigned to the $^1L_a$ state. At the same time, the peak around 320 nm originated from $^1L_b$ state was enhanced.

Fig. 7 displays the emission spectra of TP nanocrystals, compared with those of the dilute solution and bulk crystals at room temperature. As shown in Fig. 7, the emission peak positions of TP nanocrystals are almost at the same wavelengths within the experimental errors, but are slightly blue shifted from that of TP bulk crystals (dotted line) despite the similarity between their shapes. According to Swiathowski and Menzei's calculation [15], the change of twist angle of TP molecule will induce the change of the lowest singlet excited state, $S_1$, which is related to the position and shape of emission spectra. It has been established that TP molecules are planar in crystals at room temperature [14]. Thereby, it can be concluded that TP molecules align gradually in the soft lattice as they aggregate to form nanocrystals, and take a planar structure inside nanocrystals with increasing crystal size. This leads to the evolution in the optical properties of TP molecules from monomers to

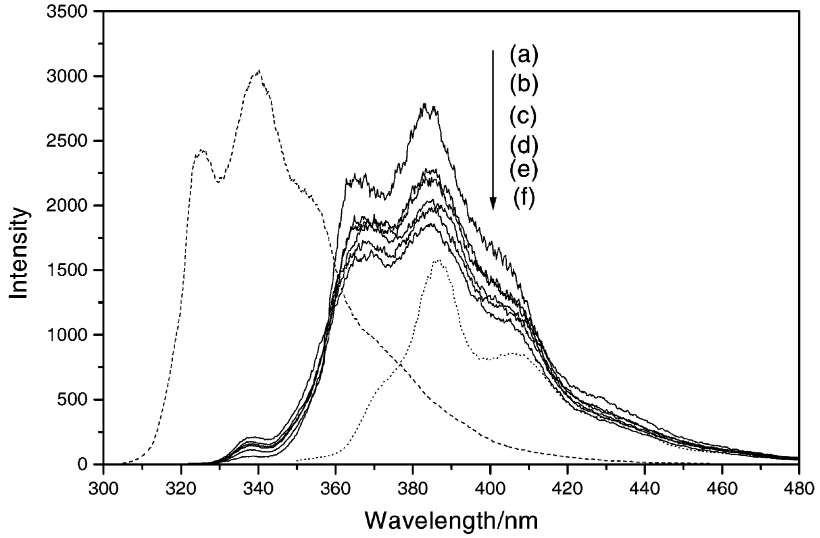


Fig. 7. Fluorescence emission spectra of TP nanocrystals dispersed in water with different sizes: (a) 50 nm, (b) 80 nm, (c) 150 nm, (d) 200 nm, (e) 250 nm, (f) 300 nm. Dashed line: the emission spectrum of TP/ethanol solution ($3.9 \times 10^{-5}$ mol l$^{-1}$). Dotted line: the emission spectrum of TP bulk crystals.

nanocrystals and to bulk crystals. The constant of the emission peak positions in the series of TP nanocrystals suggests that the planar configuration of TP molecules hardly change while nanocrystals grow.

Actually, the lowest excited state of TP nanocrystals is Frenkel-like excitons, similar to excitons formed in ultrathin organic films grown by OMBD [16]. A Frenkel exciton has small radius and is correlated to electron–hole pair localized on a single molecule. In this sense, the excited state or Frenkel excitons have little interaction with each other in the nanocrystals and the energy of Frenkel excitons has no changes in the process of crystal growth. Thus, the change of emission spectra with different crystal sizes could not be observed. This suggests that the character of the emission spectra is only related to the configuration of the TP molecule.

## 4. Conclusion

TP nanocrystals with a series of crystal sizes were successfully prepared through reprecipitation method. Their absorption peaks of $^1L_a \leftarrow {}^1A$ transition were observed to shift to the lower energy side with increasing crystal size. A new peak also emerged during this process and can be attributed to the $^1L_b \leftarrow {}^1A$ transition. The red-shift of these two peaks in the process of crystal growth may be caused by molecular association and the interaction between the TP molecules. The fluorescence excitation and emission spectra of these nanocrystals were also investigated. The excitation spectra have size-dependent property similar to absorption spectra. And the difference between nanocrystal emission and monomer emission is owing to molecular configuration. These interesting phenomena related to size effect of organic nanocrystals should attract more attention. Because there are diverse functional organic substances, full understanding of these phenomena will contribute to the application of organic nanocrystals in photoelectrical, photoconductive and other devices.

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