

Optical Properties of 4-(Dicyanomethylidene)-6-(4-dimethylaminostyryl)-2-methyl-4H-pyran Nanoparticles Prepared by Reprecipitation

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Nanoparticles of 4-(dicyanomethylidene)-6-(4-dimethylaminostyryl)-2-methyl-4H-pyran (DCM) red fluorescent dye were prepared using a reprecipitation method. The absorption spectra of DCM nanoparticles showed that compared to the absorption spectrum of a diluted solution, the intramolecular CT peak was blue-shifted due to H-aggregation. In addition, the fluorescence quenching of DCM nanoparticles was observed, resulting from H-aggregates and the twisted conformations of chromophores in the nanoparticles.

In recent years, a lot of attention has been drawn to the nanostructure study of small-molecule organic properties as well as their potential applications in nanodevices.^{1,2} Especially, nanoparticles (NPs) of small-molecule organic materials have stimulated lots of interest because of their size-dependent optical properties and flexible applications in various fields, e.g. optoelectronics, nonlinear optics, photocatalysts, and photonics.³ Some groups have embarked on systematic research on NPs of small-molecule organic materials. Nakanashi and co-workers have investigated fabrication and optical characteristics of NPs of some organic compounds such as perylene⁴ and 1,1,4,4-tetraphenyl-1,3-butadiene (TPB).⁵ More recently, Yao et al. reported optical properties of some pyrazoline derivatives.⁶ However, only a few classes of NPs of small-molecule organic materials have been studied so far.

4-(Dicyanomethylidene)-6-(4-dimethylaminostyryl)-2-methyl-4H-pyran (DCM), a well known laser dye, has been widely applied in organic light-emitting devices as a red dopant.⁷ Recently, very interestingly, tunable light emission⁸ from 1,3,5-triphenyl-2-pyrazoline (TPP) nanoparticles doped with DCM and fluorescence modulation⁹ from composite nanoparticles, based on 5-methoxy-1,3,3-trimethyl-9'-hydroxyspiroindolenaphthoxazine (SO), DCM, and 1,3-bis(pyrenyl)propane (BPP) have been obtained. To the best of our knowledge, little attention has been paid to the fabrication and optical properties of pure DCM nanoparticles. Herein, we report fabrication and optical properties of DCM nanoparticles.

DCM was purchased from Acros and used without further purification. DCM nanoparticles were prepared by reprecipitation as follows:^{4,6} 100 μL of DCM/tetrahydrofuran (THF) solution ($5 \times 10^{-4} \text{ mol L}^{-1}$) was injected rapidly into 5 mL of water with vigorous stirring, using a 100 μL microsyringe. After stirring for 5 min, the sample was left undisturbed for about 1 h to stabilize.

In this work, the obtained nanoparticles dispersed in water exhibited a light red and remained stable for one week, which is ascribed to the negative ζ potential from cyano groups in the nanoparticles.^{3a} Typical scanning electron microscopy (SEM) image of the resulting nanoparticles is shown in Figure 1a. It can

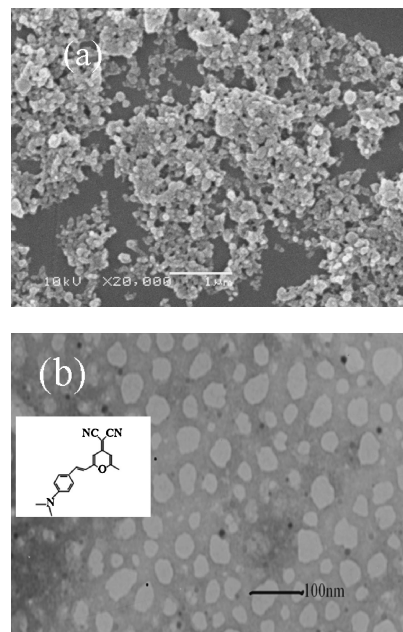


Figure 1. Microscopic images of DCM nanoparticles: (a) SEM image and (b) TEM image (small black dots are residual of staining agent, it is used to enhance image quality). Inset in (b) shows the molecular structure of DCM.

be seen that the nanoparticles are approximately particle shape with an average size of 50 nm. The transmission electron microscopy (TEM) image (Figure 1b) is consistent with the SEM. The results of selected area electron diffraction (SAED) patterns (not shown here) indicate that DCM nanoparticles are unambiguously amorphous.

The formation process of DCM nanoparticles is similar to that of perylene nanocrystal.^{4c} When DCM molecules dissolved in a good solvent (THF) are rapidly injected into a poor solvent (water), owing to the solvophobic tendency between DCM molecules and water, only a small amount of DCM molecules dissolved in water. In contrast, other DCM molecules rapidly form clusters, then the clusters aggregate to form the initial nanoparticles, under vigorous agitation. Subsequently, the metastable intermediates (the clusters and initial nanoparticles) would grow or aggregate to form DCM nanoparticles.

Figure 2 displays the UV-vis absorption spectra of as-prepared nanoparticles dispersed in water, dilute DCM/THF solution, and bulk solid of DCM. The spectrum of the dilute DCM/THF solution has a maximum absorption peaking at 497 nm, which originates from intramolecular charge transfer (CT).¹⁰ Apparently, the absorption spectrum of DCM nanoparticles shows that the intramolecular CT peak is blue-shifted

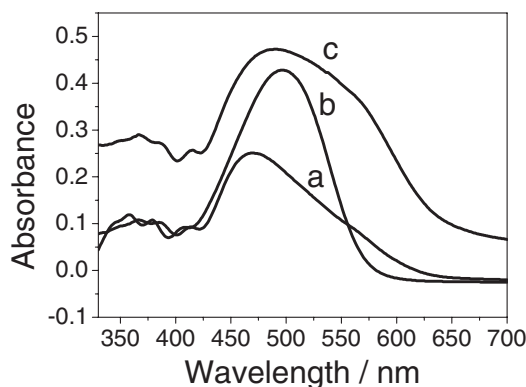


Figure 2. UV-vis absorption spectra of the samples: a) DCM nanoparticles, b) DCM/THF dilute solution (1×10^{-5} mol L⁻¹), and c) bulk solid of DCM.

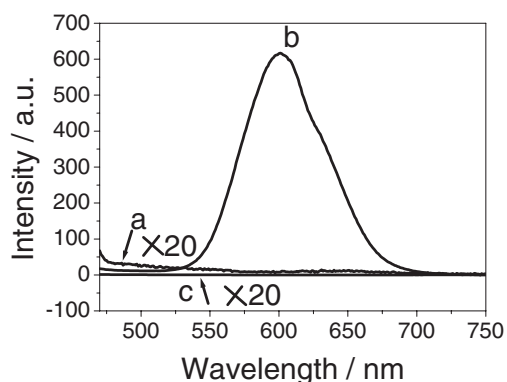


Figure 3. Fluorescence emission spectra of the samples: a) DCM nanoparticles, b) dilute solution (1×10^{-5} mol L⁻¹), and c) bulk solid of DCM.

compared with that of the diluted solution. This indicates the formation of H-aggregates in the nanoparticles.¹¹ Meanwhile, the absorption spectrum of the bulk solid of DCM presents a wide absorption band between 420 and 630 nm (Figure 2c). In addition, the tailing edge of absorption spectra at long wavelength of the bulk solid and nanoparticles becomes pronounced due to Mie scattering.¹¹

Figure 3 shows the fluorescent spectra of three samples. There is a significant difference in the fluorescence emission spectrum of nanoparticles from those of DCM/THF dilute solution and bulk solid. The dilute solution exhibits strong photoluminescence with one peak centered at 601 nm, which is attributed to transition from intramolecular CT. However, fluorescence quenching is found in the bulk solid and nanoparticles (both magnification at 20 times). It is well known that fluorescence quenching of the bulk solid of DCM is ascribed to a multitude of molecular aggregation in the bulk solid.^{7a} According to recent work, fluorescence quenching of DCM nanoparticles mainly results from two factors. One is due to the formation of H-aggregates in the nanoparticles,¹² which has been confirmed by UV-vis absorption spectra. The other is the twisted conformations of chromophores in the nanoparticles,^{3a} which tend to suppress the radiative process, as the twisted conformations of chromophores is very easily formed in DCM molecules when intermolecular forces change.¹³

In summary, 50 nm DCM nanoparticles were synthesized via a reprecipitation method. Optical properties of the nanoparticles were found different from both the dilute solution and bulk solid DCM. The results showed that intramolecular the CT absorption peak of the nanoparticles was blue-shifted compared to that of the diluted solution and fluorescence quenching formed in the nanoparticles. Work using the obtained DCM nanoparticles to fabricate optoelectronic devices is under way.

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