

Synthesis and characterization of perylene nanoparticles

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Nanoparticles were prepared in different experimental conditions by a re-precipitation method by use of perylene and polyvinylalcohol as active material and stabilizer, respectively. The excitation and emission spectral properties of dispersions in aqueous solutions of the various samples were recorded together with the fluorescence quantum yields and lifetimes (where detectable). The experimental results are consistent with the formation of excimer-like states, responsible of the emission properties, in the nanoparticles. Confocal fluorescence and atomic force (AFM) microscopies were able to give information on the fluorescence properties and size distribution (most probable size of 3–5 nm) of the nanoparticles.

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1 Introduction

Nanoparticles are interesting nanostructured materials since they exhibit unique optical and chemical properties which differ from isolated molecules and bulk solid state [1–4].

In the case of inorganic semiconductor and metal nanoparticles, it has been well established that their optical properties strongly depends on the particle size, owing to the quantum confinement of the excitons [4, 5] which can easily be generalized independently of the chemical nature of the particles.

Although quite some research work has been done [1, 6, 7], for the organic nanoparticles it is still not clear which is the size effect on the optical and chemical properties. In some cases, it has been found a correspondence between spectral shifts and particle sizes [2, 8]. However, it seems quite difficult to generalize their optical and chemical behaviour since it depends on several properties such as the electronic properties of the starting compounds, the ground state conformation [2] and the ability to form ordered aggregates [9]. When the active material is made of aromatic molecules, it is clear that the particle size can be affected by external factors, e.g. stabilizer concentration, [10] but it is not yet clarified how the emission properties can be tuned.

In this research work, perylene was used as active material to prepare nanoparticles through the precipitation method [7], in different experimental conditions, in order to test the tunability of the particle properties (size and spectra).

2 Experimental section

The particles were prepared with perylene (Sigma, spectro-grade) as active material and polyvinylalcohol (PVA, Fluka) as stabilizer. The synthesis of the particles was carried out with the re-precipitation method [7]. In particular, 1.2 ml of a perylene solution in acetone (7×10^{-4} M) was injected in 30 ml of an aqueous solution (final concentration 2.8×10^{-5} M) where PVA (6 mg/ml) was previously dissolved.

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It has to be noted that the perylene and PVA concentrations were optimised to obtain small particles with reproducible properties and with a high fluorescence efficiency. In particular, the concentration of perylene in the aqueous solutions was changed in the $0.1\text{--}9 \times 10^{-5}$ M range and the amount of PVA was modified up to 60 mg/ml. By using the optimized concentrations, the nanoparticles were also prepared at different temperatures by adding the perylene acetone solution to the aqueous PVA solution thermally equilibrated at 273, 298 and 353 K.

The absorption spectra of the samples were recorded by a spectrophotometer (Perkin Elmer, Lambda 800). A spectrofluorimeter (Spex Fluorolog) was used to record corrected emission and excitation spectra of the samples by using the “front face” configuration. The spectra were corrected for the response of instrument components at each wavelength. The fluorescence quantum yields of the samples (mean deviation of three independent measurements $\sim 7\%$) were determined from the emission spectra by using anthracene in ethanol as standard [11].

Fluorescence lifetimes, τ_F (mean deviation of three independent measurements $\sim 10\%$) were measured by a Spex Fluorolog- $\tau 2$ system, which uses the phase modulation technique (excitation wavelength modulated in the 1–300 MHz range; time resolution ca. 20 ps).

Samples for the microscopy investigations were prepared by spin coating the suspensions on cover glasses or mica.

The fluorescence images were recorded through a laser scanning confocal microscope (Nikon, PCM2000) using an Ar-laser ($\lambda_{\text{exc}} = 488$ nm) as light. The images were obtained with a 60 \times , 1.4 N.A. oil immersion objective (512×512 pixels).

An atomic force microscope (Solver-Pro, NT-MDT) was used to record topography and phase images. The measurements were carried out in semicontact conditions by use of 190–325 kHz cantilever having 10 nm radius. A grain analysis was carried out to determine the size distribution of the particles from the images.

3 Results and discussion

The synthesis of the nanoparticles was carried out with the method reported in the literature [7] which consists in the injection at room temperature (293 K) of a perylene solution in acetone in water (Milli-Q) where a protecting agent as polyvinyl alcohol (PVA) was previously dissolved. The spectral properties of perylene particles are markedly different from those observed in homogeneous organic media; in particular, Fig. 1 shows the absorption and the emission spectra of perylene in acetone and in aqueous dispersion in the presence of PVA. The fine structure observed in the spectra of molecular perylene is lost when perylene is dispersed in water and it is replaced by a broad absorption band with the main maxi-

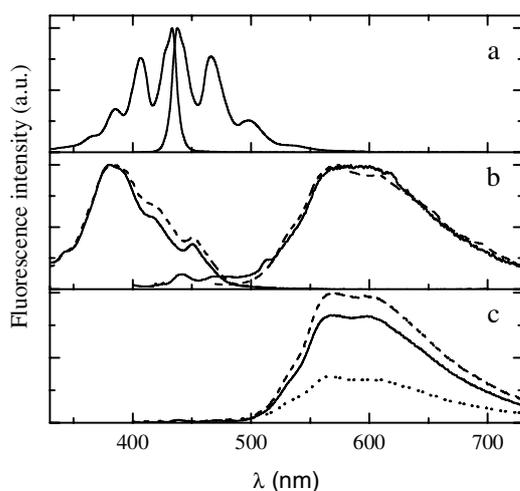


Fig. 1 Emission and excitation spectra of a) perylene in acetone and b) perylene particles with PVA (solid line) and without (dashed) and c) perylene particles prepared at 273 K (dashed line), 298 K (solid line) and 353 K (dotted line).

Table 1 Fluorescence parameters of perylene nanoparticles prepared at different temperatures.

temperature (K)	ϕ_F	τ_F (ns)
273	0.18	12.4
298	0.15	13.0
353	0.047	

mum at 385 nm and a pronounced shoulder at 452 nm. The effect of particle formation on the emission spectra is even more evident since besides the structure loss a marked red shift is observed ($\lambda_{em} = 438$ nm and 570 nm in acetone and aqueous suspensions, respectively).

These findings are in agreement with literature data for similar samples [1, 7] where similar effects are attributed to the formation of nanostructured materials. As reported in the literature, the low solubility of perylene in aqueous media induced the formation of perylene aggregates which likely act as a start point for particle nucleation; the presence of PVA allows the growth/coalescence of the nuclei to be controlled. The spectral behaviour of the particles resembled those observed for perylene excimers [12]. The particle emission, in comparison with the photophysical properties of perylene molecules, was used to characterize the dispersed material in order to achieve a better understanding of the interactions driving the particle formation and stabilization. In fact, the emission quantum yield (ϕ_F) of the nanoparticles (Table 1) is 0.15, to be compared with that obtained for perylene in homogenous environment ($\phi_F = 0.75-0.8$ [11]).

Thus, the radiative deactivation path of nanoparticles is less efficient, probably due to the occurrence of strong interactions between the perylene molecules that alter the properties of the emitting state. By use of phase shift method the fluorescence decay time (τ_F) of the particles was measured obtaining different results upon changing the emission detection conditions. When the luminescence was selectively recorded (either through a monochromator or band pass filters) at wavelengths above 560 nm the fluorescent curves were satisfactorily fitted by a mono-exponential function giving a τ_F value of 13.1 ns, while the fluorescent kinetics recorded at lower wavelengths were fitted by a bi-exponential function with the long component (13.1 ns) due to the particles and the shorter one (5.6 ns) assignable, in agreement with literature data, to the “free” perylene molecules; the relative amplitude of the two components changed with the emission wavelength. This observation indicates that the water dispersion is actually a mixture of free perylene molecule and aggregates.

To get information on the morphology of the dispersed material, confocal fluorescence measurements have been carried out upon deposition of the water dispersion through a spin coated on cover glasses. The images revealed that the fluorescent material was organized in particles having size below 1 μm (Fig. 2a) and a spherical shape as demonstrated by z-scan acquisitions. Furthermore, the fluorescence distribution was quite homogenous within a single particle suggesting that the perylene molecules

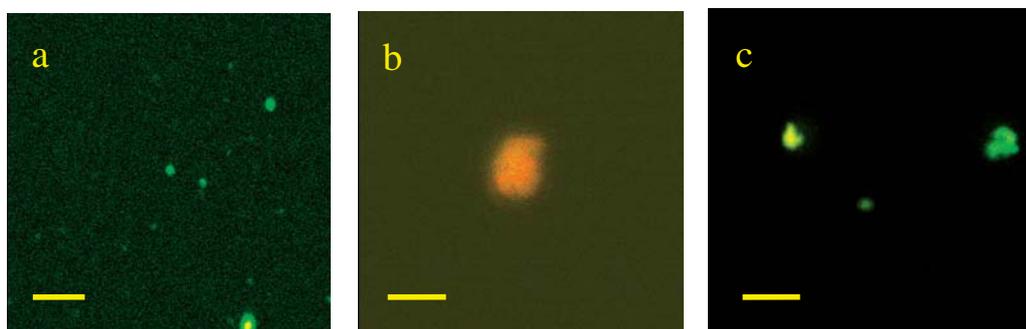


Fig. 2 (online colour at: www.pss-a.com) Fluorescence images of perylene nanoparticles prepared at a) 298 K with PVA (space bar corresponding to 5 μm), b) 298 K without PVA (space bar corresponding to 10 μm) and c) 358 K with PVA (space bar corresponding to 40 μm).

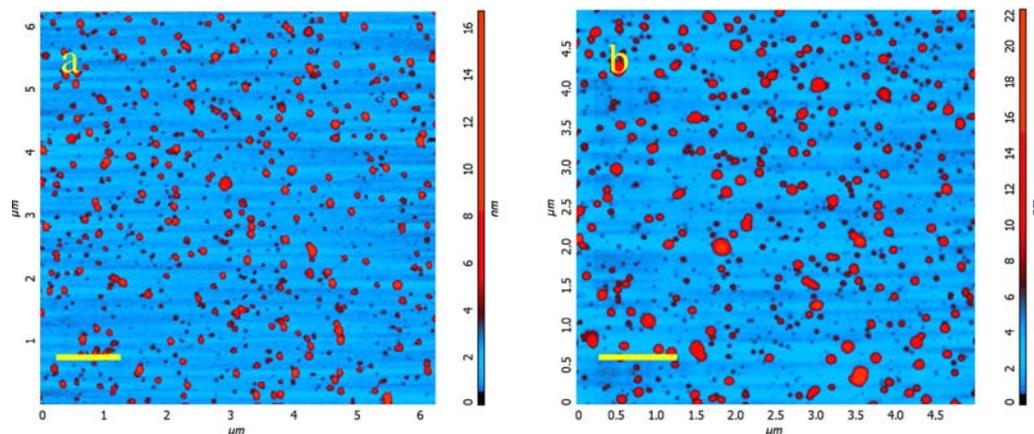


Fig. 3 AFM images of perylene nanoparticles with PVA prepared at a) 298 K and b) 273K (space bars corresponding to 1 μm).

are homogeneously distributed in the particle and have similar photophysical parameter. Besides the big and bright particles, the images revealed the presence of smaller ones with dimensions of about 300 nm; taking into account the spatial resolution of the experimental setup, their size could be much smaller.

AFM images were recorded from the same samples investigated by the confocal microscope and confirmed the presence of spherical particles and that the majority of them was below 10 nm height (Fig. 3a). The grain analysis carried out on the images recorded on the samples prepared at 298 K (Fig. 5a) indicates that the most probable particle size is about 5 nm. Only occasionally particles with height similar to the dimensions measured by the confocal microscope were found; this can be explained considering the lower spatial resolution of the confocal microscope which can easily detect and characterize only the particles at the tail of the distribution. These observations show that particles with size in the nanometer range can be prepared by the re-precipitation method, however the particles do not present a unique size but they are better defined by a size distribution.

Particles were prepared in different experimental conditions to elucidate the influence of the external and microenvironment factors on their optical and morphological properties.

The particles prepared without addition of the stabilizer (PVA) showed spectral properties similar to those obtained from the particles with PVA (Fig. 1b) however their fluorescence quantum yield was five times lower (0.031) than in the presence of PVA. On the other hand, the dimensions of the particles

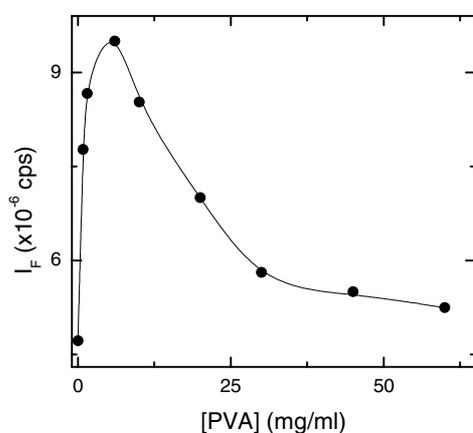


Fig. 4 Effect of PVA concentration on the emission intensity of perylene nanoparticles ($\lambda_{\text{exc}} = 380$ nm and $\lambda_{\text{em}} = 570$ nm).

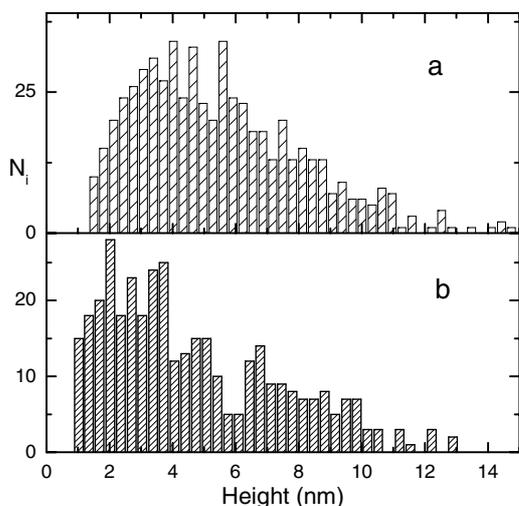


Fig. 5 Histograms of size distributions obtained from the AFM images of perylene nanoparticles with PVA prepared at a) 298 K and b) 273 K.

without PVA were bigger than those prepared in the presence of the stabilizer since diameter up to 10 μm were measured by confocal microscopy (Fig. 2b). These observations suggested that the increase in dimensions can be attributed to the absence of PVA which would not stop the particle growth and/or their coalescence. Furthermore in the present experiment the increase in dimensions did not correspond to spectral changes as reported in the literature for similar samples [2, 7]. However, the emission intensity (I_F) of the nanoparticles was strongly affected by the PVA concentration (Fig. 4). The intensity increased upon addition of PVA reaching a maximum value in correspondence of 6 mg/ml and then decreased for further additions as shown in Fig. 4. Actually the amount of stabilizer was optimized on the basis of fluorescence efficiency of the nanoparticles.

Particles with PVA were also prepared at different temperatures (273, 298 and 353 K) show a similar spectral behaviour (Fig. 1c); however the fluorescence efficiency was strongly dependent on the synthesis conditions. In particular, the particles prepared at lower temperature have the highest value (0.18) while the sample prepared at 353 K has a much lower ϕ_F (0.047). On the other hand the τ_F values of about 13 ns (Table 1) were detected for the particles, independently from the preparation temperature (at least for the samples where the fluorescence efficiency was high enough to allow τ_F to be measured). The emission of the particles is likely coming from an excimer-like state; in fact, the fluorescence spectra and lifetimes remain constant despite of the preparation conditions. Instead, the change of ϕ_F should indicate the different amount of emitting excimers formed in the various experimental conditions.

Microscopy investigations revealed a strong effect of the preparation temperature on the dimensions of the particles. Confocal fluorescence images recorded from the samples prepared at 358 K showed the presence of aggregates with irregular shape and dimensions in the range 2–9 μm . AFM images (not shown) confirmed that these samples are characterized mainly by big-size particles. In the case of samples prepared at 273 K the morphological investigations indicated that the distribution of particle size moved to lower domains. Confocal fluorescence images show the presence of particles with diameter below 0.7 μm ; however, most of the fluorescent spots were too small to be dimensionally resolved by the optical microscope. AFM images showed that the samples were characterized by well defined spherical particles with a few nm-height (Fig. 3b). In particular the grain analysis pointed out that the particles were not uniform but distributed over a certain range; however the most probable height was about 3 nm.

In conclusion, using perylene as active material and PVA as stabilizer, particles of few nanometers height characterized by an emission spectrum and a fluorescence lifetime related to a perylene-excimer state and by a morphology described by a size-distribution more than a unique dimension were obtained by the re-precipitation method. Differently from what reported in the literature for other organic particles [1, 2], the preparation conditions of these perylene nanoparticles can modify the size distribution and the

amount of the emitting excimer-like state produced, but not the spectral properties which are size-independent (at least in the cases here investigated).

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