Supporting Information

Mechanofluorochromism of a Difluoroboron-β-Diketonate Derivative at the Nanoscale

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1. Preparation of the nanoparticles by the reprecipitation method

DFB-Bu-Amide was dissolved in THF (standard concentration $C = 5 \times 10^{-5}$ mol L$^{-1}$). A volume was collected (standard quantity 600 µL) and quickly injected in millipore water under vigorous stirring (total volume 3 mL). The mixture was stirred for 5 min at 800 rpm.

2. Photophysical studies and characterizations

2.1 Equipment

The UV-visible absorption spectra were recorded on double beam spectrophotometers Cary 100 or Cary 4000 (Agilent) equipped with deuterated/halogen lamps. The emission spectra were recorded on spectrofluorometers Fluoromax-FM3 or Fluorolog FL3-221 (Horiba Jobin-Yvon) with xenon light sources.

2.2 Fluorescence quantum yields

Fluorescence quantum yields in solution were measured using quinine sulphate in H$_2$SO$_4$ 0.5 M (literature $\Phi_F(0) = 0.54$) as the reference. All solutions were diluted (OD < 0.1). The fluorescence quantum yield of the samples $\Phi_F(x)$ were calculated using the following equation:

$$\Phi_F(x) = \Phi_F(0) \frac{1 - 10^{-A_0}}{1 - 10^{-A_x}} \frac{S_x}{S_0} \left( \frac{n_x}{n_0} \right)^2$$

with $\Phi_F(0)$ and $\Phi_F(x)$ the fluorescence quantum yield of the reference and of the sample, respectively; $S_0$ and $S_x$ are the integrated fluorescence spectra of the reference and the sample; $A_0$ and $A_x$ are the values of the absorbance of both samples at the chosen excitation wavelength; $n_0$ and $n_x$ are the refraction index of the solvent and the solution, respectively.

Powders and nanoparticles fluorescence quantum yields were obtained by using the integration sphere of the Fluorolog FL3-221 (Horiba Jobin-Yvon acquisition and analysis software).

2.3 Coverglass cleaning

The coverglasses were preliminary cleaned before the deposition of the nanoparticles by several steps of sonication in the following solvents: 1% Hellmanex water solution, acetone, ethanol, 1M sodium hydroxide water solution and distilled water, then dried with a heat gun. Eventually the coverglasses were treated by plasma cleaning for 20 seconds to remove any organic residual.
2.4 Fluorescence microscopy

The images acquired by fluorescence microscopy were recorded on an inverted microscope (Nikon, Eclipse Ti-U) in widefield mode. The samples were excited by a Lumencor Spectra X light engine at 400 nm. The fluorescence signal was collected by the objective lens (Nikon 60X/0.95 ON Plan Apo I), separated from the incident excitation beam by a Semrock LF405 dichroic mirror, and directed either to an EMCCD camera (Andor iXon Ultra 897) or to a CCD-spectrograph (Princeton Instrument Acton SP2356 with Spec-10 400Br/LN-eXcelon CCD detector). All the images were analyzed by the Solis software (Andor) and the spectra were analyzed by the Winspec/32 software (Princeton Instrument).

2.5 AFM measurements

AFM images were acquired with a JPK NanoWizard®-3 instrument. The head of the AFM was designed to be installed on the inverted optical microscope, allowing nanoparticle position, size and shape observations, to be correlated with the corresponding photophysical properties. AFM topography was recorded in tapping mode under ambient conditions. Silicon cantilevers (Nanosensors, PPP-NCHR) were used after calibration of their spring constant thanks to a thermal noise procedure included in the JPK software. The scan rate for a 512×512-pixels image is 0.6 Hz (line rate). Image analysis was performed using the JPK analysis software. The height determination was realized using the IGOR software (Wavemetrics).

To induce locally mechanical shearing stress, the same silicon cantilevers (Nanosensors, PPP-NCHR) were employed. The AFM was then used in contact mode to shear the surface of the particles with vertical forces ranging from 128 nN to 512 nN and a scan rate for a 128x128 pixels-image of 0.6 Hz (line rate).
3. Investigation of the mechanofluorochromism at the nanoscale

3.1 Green-emitting nanoparticles

![Normalized emission spectra of two isolated green-emissive nanoparticles (left: NP1, right: NP2) before mechanical stimulation (red curves) and after application of several shearing mechanical stress sequences. Shearing stress applied by means of the AFM tip in the contact mode.](image)

Figure S1.

3.2 Yellow-emitting nanoparticles

![Non-normalized emission spectra of two isolated yellow-emissive nanoparticles (left: NP1, right: NP2) before mechanical stimulation (red curves) and after application of several shearing mechanical stress sequences. Shearing stress applied by means of the AFM tip in the contact mode.](image)

Figure S2.

![AFM topography of a single yellow-emissive nanoparticle before (left) and after (right) shearing mechanical stress (130 nN) by means of the AFM tip in the contact mode.](image)

Figure S3.
4. Photographs

All the photographs were taken with a Canon 70D camera with the help of a TQC Colorbox VF0600 illumination system equipped with a UV light source (365 nm).