Electronic Supplementary Information (ESI) for PCCP
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Spectroscopy of BODIPY solid phase: crystal and amorphous nanoparticles.

Yuanyuan Liao, *[a] Valérie Génot,[a] Rachel Méallet-Renault,[a] Thanh T. Vu,[a] Jean-Frédéric Audibert,[a] Jean Pierre Lemaistre,[a] Gilles Clavier,[a] Pascal Retailleau,[b] Robert B. Pansu.[a]

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1. Experimental details.

DLS, dynamic light scattering

The Adambodipy NPs suspension was analyzed by a dynamic light scattering analyser (DL135 Particle Size Analyser, Cordouan Technologies), equipped with a 15 mW diode laser, operating at 650 nm. An original design of the sample cell is proposed to enhance the DLS instrument with back-scattered light detection, and the capability to control the sample thickness. The photo-detector collects the back-scattered laser light signal, at an angle of 135°.
We could analyse sample volume as small as 50µL. The main limitation concerns dilute suspensions (2×10^{-6}g/ml), when the signal is difficult to discriminate from noise. For the Adambodipy nanosuspension samples in water we worked at a temperature of T=20°, with viscosity 1.003cP. An acquisition lasts for 45 seconds, and is repeated 30 times. Each acquisition generates a size distribution curve using a Padé-Laplace algorithm. The 30 curves are cumulated to give a histogram of the size distribution.

AFM

The NanoWizard® 3 BioScience atomic force microscope (AFM, JPK, Berlin, Germany) is capable of high-resolution image for the crystal terrace and the nanostructure of the surface. It has been used here to image the needle shaped Adambodipy crystals. The crystal was first moved to the microscope cover slips No. 1 borosilicate glass, 0.15 mm thickness, and then repeatedly washed with water. Imaging was done in intermediate-contact mode using commercial silicon nitride cantilevers (ACTA probe, rectangular, no coating, Applied NanoStructures, Inc.) and a scan rate for a 512×512 pixel image from 0.2 to 1 Hz. Height analysis was performed using the JPK software.

Crystallization of Bodipy derivatives :

The curve of solubility of the Adambodipy molecule in organic-water mixture was obtained in the following way: 1. The partial dissolution of Adambodipy powder was done in several organic-water mixtures with percentage of water varying from 10 to 90%. After 2 days under stirring we obtained saturated mixtures – 2. The clear supernatant was then collected, analysed by spectrophotometry and compared to a calibration curve.

2. Crystallographic data and structure refinement for Adambodipy crystal

The reflections were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods with SHELX97-S program[1]and refined by full matrix least squares, based on F2, using the SHELX97-L software through the CRYSTALBUILDER interface.2 All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generated in idealized positions, riding on the carrier atoms, with isotropic thermal parameters. The final cycle refinement including 392 parameters converged to R1 = 0.0491 (4393 data with $I > 2\sigma(I)$) and wR2 = 0.1488 (all 5756 data), Goodness of Fit S=1.152, max./min. residual electron density 0.238/-0.205. CCDC reference number is 852756.

Table 1: Crystallographic data and structure refinement for Adambodipy crystal.

Formula	$C_{38}H_{45}F_2N_2$
Mr g.mol^{-1}	578.57
Space Croup	P 2_1/c
Cell Length (Å)	a 14.0557(3), b 11.4779(3), c 19.3737(13)
Cell Angles(°)	a 90.00, b 98.905, c 90.00

Volume (Å^3)	3087.9(2),
Z , Z'	Z: 4, Z': 0
ρcalcd g.cm^{-3}	1.245
m (mm^{-1})	0.626. 20448
measured reflections	(2qmax = 144.2°)
R_{int}	0.0586

3. TDDFT results for isolated molecule:

Vertical transition 1: 419 nm (23866 cm^{-1}) with oscillator strength f=0.56

TDDFT results for dimer H related to exciton splitting:
Vertical transition 3: 429 nm (23310 cm^{-1}) with f=0.28
Vertical transition 4: 413 nm (24213 cm^{-1}) with f= 0.71
Exciton splitting: 451 cm^{-1} (= (VT2-VT1)/2)

TDDFT results for dimer J related to exciton splitting:
Vertical transition 3: 422 nm (23697 cm^{-1}) with f=1.00
Vertical transition 4: 417 nm (23981 cm^{-1}) with f= 0.01
Exciton splitting: 142 cm^{-1} (= (VT2-VT1)/2)

[1] G.M. Sheldrick, *Acta. Cryst,* 2008. **A**64, 112-122.

[2] R. Welter, *Acta Cryst.* 2006. A62, s252.