Journal of the American Chemical Society 2018 vol.140 N46, pages 15827-15841

# Mapping Forbidden Emission to Structure in Self-Assembled Organic Nanoparticles

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## Abstract

© 2018 American Chemical Society. The interplay between micromorphology and electronic properties is an important theme in organic electronic materials. Here, we show that a spirofluorene-functionalized boron-dipyrromethene (BODIPY) with an alkyl norbornyl tail self-assembles into nanoparticles with qualitatively different properties as compared to the polymerized species. Further, the nanoparticles exhibit a host of unique emissive properties, including photobrightening, a blue satellite peak, and spectral diffusion. Extensive photophysical characterization, including single-particle imaging and spectroscopy, and time-resolved fluorescence, coupled with electronic structure calculations based on an experimentally determined crystal structure, allow a mechanism to be developed. Specifically, BODIPY chromophores are observed to form quasi-two-dimensional layers, where stacking of unit cells adds either J-aggregate character or H-aggregate character depending on the direction of the stacking. Particularly strongly H-coupled domains show the rare process of emission from an upper exciton state, in violation of Kasha's rule, and result in the blue satellite peak. The spatial heterogeneity of structure thus maps onto a gradient of photophysical behavior as seen in single-particle imaging, and the temporal evolution of structure maps onto fluctuating emissive behavior, as seen in single-particle spectroscopy. Taken together, this system provides a striking example of how physical structure and electronic properties are intertwined, and a rare opportunity to use one to chart the other.

http://dx.doi.org/10.1021/jacs.8b09149

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