Polymorphs of single organic compound provide insight into structure-spectra relationships

Conjugated organic compounds hold great promise for the manufacture of thin, flexible displays, cost-effective solar cells, and low-power household-scale optical communications—if they can be developed for passive and active components. Solid-state organic lasers, which have a broad photoluminescence spectrum that is tunable over a wide wavelength range, a high gain coefficient, and the potential for self-waveguiding, are particularly important. Developing materials for these applications requires an understanding of the relationship between the molecular conformations, their crystalline packing, and the emission properties. However, in most crystalline polymorphs, the conformation and packing vary simultaneously.

Now—as described in the September 17 issue of *Advanced Materials* (DOI: 10.1002/adma.20140114; p. 6168)—a research team at Jilin University in China has reported the growth and stimulated emission characteristics of several luminescent polymorphs of a single organic compound in which molecular conformation and packing vary independently.

"Our group has been interested in designing simple molecular systems that can precisely disclose the influence of the molecular conformation or packing on the luminescent properties of the materials," said Hongyu Zhang, one of the lead researchers.

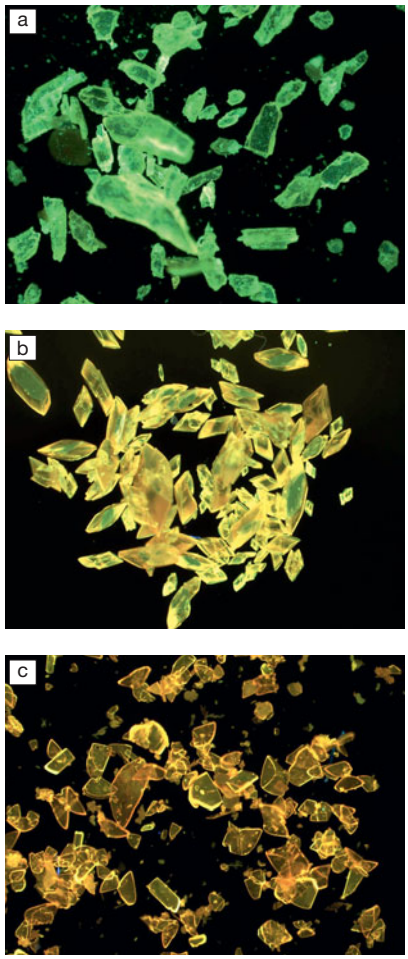
The researchers used different crystal growth conditions to produce four polymorphs—fluorescing green, green-yellow, yellow, and orange, respectively—of 4,4′-(thiazolo[5,4-*d*]-thiazole-2,5-diyl)bis (*N*,*N*-diphenylaniline). "This compound has been employed as an active material in OPV [organic photovoltaics]. Another possibility regarding the practical application of this molecule is as an emitting material in OLEDs [organic light-emitting diodes]," Zhang said. The molecule includes three π-conjugated units connected by carbon-carbon single bonds. Rotation about the C-C single-bond axis varies the overlap of the π-electron clouds associated with each of the conjugated subunits.

Two polymorphs, green and green-yellow, are conformational isomers with different degrees of π-electron conjugation. In the third, the yellow version, the molecules are packed more tightly within the crystal, which strengthens the intermolecular interactions in that polymorph. The orange polymorph, in contrast, contains a loose-packed mixture of conformations, such that there are essentially no intermolecular interactions. This set of structures therefore offers two polymorphs that have the same conformation but different crystalline packing, and two which have the same packing but differing torsion angles between the π-conjugated units within the molecule. Zhang, Wang, and their team found that the molecular conformation does not affect the quantum yield, while intermolecular overlap does. Strong intermolecular interactions, in turn, increased the fluorescence lifetime.

The slab-like crystalline shape and high quantum yield of one polymorph led the researchers to investigate the lasing behavior of the materials. They were able to stimulate amplified spontaneous emission (ASE) in the green polymorph, as well as in the mixed (orange) version. Two other polymorphs showed no ASE; their block-like crystalline form may not permit the waveguiding necessary to keep the emitted photons within the gain medium long enough to be amplified by stimulated emission. Zhang, Wang, and team thus demonstrated the effect of molecular conformation and packing on emission properties.

"I believe our results not only provide a general theory about structure-spectra relationships, but also give guidance in designing molecules with desired emissions spectra," said Zhang.

Jen Gordon



Three colored polymorphs of the reported compound. (a) and (b) have similar molecular packing but different molecular conformations; (b) and (c) have similar conformations but different packing within the crystal.

Addendum

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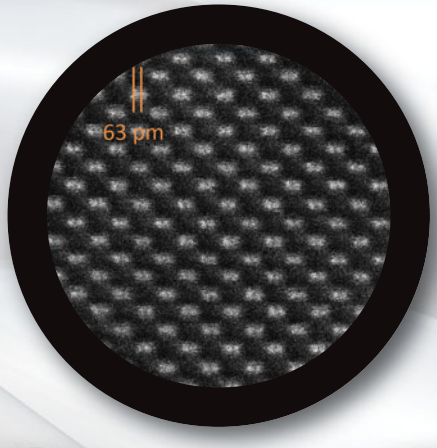

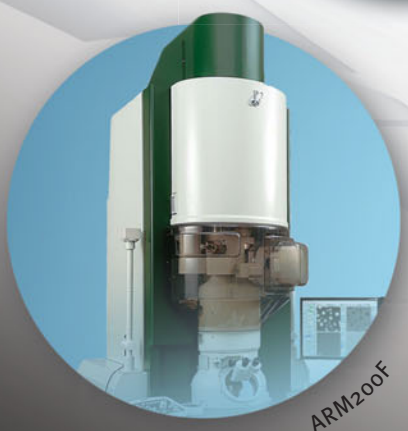
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