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Communication

Strong optical nonlinearities of self-assembled polymorphic microstructures of phenylethynyl functionalized fluorenones

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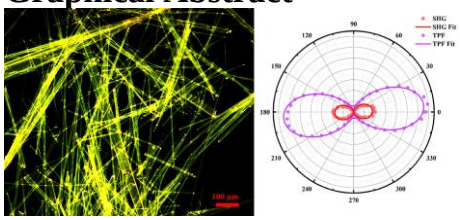
Graphical Abstract



The polymorphs of a phenylethynyl functionalized fluorenone derivative, and their controlled self-assembly for microstructures with different morphologies have been studied. These polymorphic microcrystals exhibit very distinctive NLO properties, which are highly correlated to their electronic and supramolecular structures.

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ABSTRACT

Highly efficient nonlinear optical (NLO) materials with well-defined architectures in the wavelength and subwavelength length scales are of particular importance for next generation of integrated photonic circuits. Fluorenone analogues have been demonstrated to be promising candidates as building blocks for assembly of organic NLO materials thanks to their synergistic supramolecular interactions and brilliant optical properties. Here we have studied the polymorphs of a phenylethynyl functionalized fluorenone derivative, and their controlled self-assembly for microstructures with different morphologies. These polymorphic microcrystals exhibit very distinctive NLO properties, highly related to their supramolecular and electronic structures.

Highly efficient nonlinear optical (NLO) materials play essential roles not only in advanced modern technologies ranging from super-resolution microscopy and lithography to terahertz (THz) generation, but also in many daily life aspects such as telecommunication, signal processing and data storage [1,2]. In particular, NLO materials with well-defined architectures on the (sub)wavelength length scales are regarded as the key materials for developing the next generation integrated photonic circuits [3-5]. Second harmonic generation (SHG) [6] is one of the most widely studied and used second-order NLO effects, in which two photons of incident light combine and generate a photon with doubled frequency and energy. It is usually generated when an intense pulsed laser beam interacts with a medium that has a high NLO hyperpolarizability, β, and equal importantly, a non-centrosymmetric geometry [7]. Two-photon excited fluorescence (TPF), on the other hand, is a nonlinear optical up-conversion process described by a third-order nonlinear optical two-photon absorption (TPA) mechanism [8]. Despite that inorganic NLO materials such as barium borate (BBO), Zinc oxide (ZnO), and potassium dihydrogen phosphate (KDP) are well-established and widely used, organic NLO materials have been demonstrated to have various advantages, including high hyperpolarizabilities, structure diversities and eases of process [9-11]. In particular, the tailor-made molecular structures of organic NLO dyes allow for hierarchical self-assembled architectures on the micro- and nano- scales by multiple supramolecular interactions [3,12,13]. This results in subwavelength scale materials with very well-

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