



The solvent-induced morphological changes of organic microstructural materials: Morphology-sensitive photophysical properties

LiuSong Ni, Chen Shen, GuoPing Yong*

Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

HIGHLIGHTS

- Organic microstructural materials fabricated by solid-phase anion exchange reactions.
- The solvent-induced morphological changes.
- Solvent type (protic/aprotic)/polarity can significantly tune the morphologies.
- The sheetlike morphologies reveal enhanced photophysical properties.
- Unusual three-dimensional hexangular prismlike or cubelike morphologies.

ARTICLE INFO

Article history:

Received 29 November 2016
 Received in revised form
 30 October 2017
 Accepted 13 November 2017
 Available online 15 November 2017

Keywords:

Boron-difluoride complex
 Organic microstructural materials
 Solvent effect
 Morphology
 Photophysical property

ABSTRACT

The research reported herein demonstrates the great effects of solvent type (protic/aprotic)/polarity on morphologies of boron-difluoride complex microstructural materials. We found that the hydrogen bonding interaction between protic solvent (water or ethanol) and boron-difluoride complex could subtly tune the anisotropic growth to give sheetlike morphologies. However, the aprotic dipole solvent (acetonitrile or acetone) mainly induces unusual hexangular prismlike or cubelike morphologies. It is interestingly found that the solvent polarity also has important influence on morphologies. Compared to prismlike or cubelike morphologies, microsheet morphologies reveal enhanced luminescent emission and near-infrared absorption, which should be attributed to morphological anisotropy, demonstrating morphology-sensitive photophysical properties. This work exemplifies that solvent type (protic/aprotic)/polarity can significantly tune the morphologies and properties of organic micro/nanomaterials.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Organic micro/nanomaterials have drawn more attentions due to their interesting properties and potential technological applications such as optoelectronics, catalysis, energy storage, and sensor [1–5]. Because morphology and size of organic micro/nanostructures play an important role in determining their properties, the developing a facile fabrication strategy is important to explore the effects of the morphology/size on their properties. Organic micro/nanomaterials with various morphologies such as particles, rods, wires, sheets, cubes and fibers, have been fabricated by using different approaches [6–15]. However, the morphology/

size-controllable fabrication of organic micro/nanomaterials is still a challenge. Therefore, there is an increasing interest in developing preparation methods to control the morphology of organic micro/nanostructural materials, in which solid-phase reaction is a facile and green strategy to fabricate organic microstructural materials [16–18].

The organic micro/nanomaterials with various morphologies are easily self-assembled through supramolecular interactions [19]. Other conditions such as reaction rate, pH value, ultrasound, and solvent, etc. [20–26], have also a remarkable effect on the self-assembled micro/nanostructures. In particular, the solvent molecule is crucial for regulating the thermodynamic assembly process. Thus, solvent can help to balance the solubility and crystallization of solute molecules, and change the assembled mode of solute molecules through solute-solvent interactions [25,26]. Li and co-workers reported the fine-tuned nanostructures can be

* Corresponding author.

E-mail address: gpyong@ustc.edu.cn (G. Yong).

assembled from bisimide derivatives through changing the solvent polarity and concentration [27]. By changing the solvent polarity and solute concentration, they obtained various nanostructures, including nanospheres, nanowires, nanobelts and nanosheets. Miao et al. systematically studied solvent-induced self-assembly of 2,7-ditridecyloxy-9-fluorenone, which morphologies were controlled also through varying the solvent and solution concentration [28]. Zhang and co-workers found that the interactions between the pyridylpyrazole headgroups and the solvents could regulate the stacking of the molecules and self-assembled nanostructures [29]. Mahaling and Katti reported the effects of solvent type on microstructures of polymer [30]. Krukiewicz et al. studied the effect of solvent on physicochemical properties of poly(3,4-ethylenedioxyppyrrrole) [31].

Recently, we reported morphology-controllable fabrication of boron-difluoride (BF_2) complex microcrystals by facile solid-phase anion exchange reactions [18]. Herein, we present the effects of solvent type (protic/aprotic)/polarity on morphologies of BF_2 complex microstructural materials. It is interestingly found that the solvents have important influence on morphologies, especially, the aprotic dipole solvent even can induce unusual hexangular prismlike or cubelike morphology. We also demonstrate that morphological changes exhibit obvious effect on the photophysical properties. The major purpose of this work is to unveil that morphological properties of organic micro/nanomaterials are tunable by solvent type and/or polarity.

2. Experimental

2.1. Material and methods

The solid-state UV/Vis/NIR absorption spectra were recorded at room temperature on a DUV–3700 UV/Vis/NIR spectrometer. The solid-state photoluminescence spectra were determined at room temperature on a Fluorolog-3-TAU fluorescence spectrophotometer. Powder X-ray diffraction (PXRD) patterns were collected on a Philips X'pert PRO SUPER diffractometer operating with nickel-filtered $\text{Cu-K}\alpha$ radiation ($\lambda = 1.540598 \text{ \AA}$) at 40 kV and 200 mA. Field-emission scanning electron microscopy (FE-SEM) measurements were performed with a FEI Sirion 200 field emission scanning electronic microanalyser operated at accelerating voltage of 5 kV.

2.2. Preparation of microstructural materials

The BF_2 complex ($\text{BF}_2\text{-HbipoCl}$) was prepared from $\text{BF}_2\text{-bipo}$ by simple vapor-solid protonation reaction with HCl vapor, according to the previous procedure [17]. $\text{BF}_2\text{-HbipoPF}_6$ and $\text{BF}_2\text{-HbipoSCN}$ microstructural materials were fabricated as follows: $\text{BF}_2\text{-HbipoCl}$ (1.34 g, 4.00 mmol) was immersed to 20 mL various solvents such as water, acetonitrile, ethanol, or acetone. To the stirred system, the saturated KPF_6 or KSCN (7.0 eq.) aqueous solution was dropwise added. The resulting solid-phase anion exchange reaction system was stirred for 30 min at room temperature, then filtered off, washed several times with fresh deionized water, and then dried in air at 75°C for 8 h.

3. Results and discussion

When using various solvents, solid-phase anion exchange reactions between $\text{BF}_2\text{-HbipoCl}$ and PF_6^- anion [18] afforded four $\text{BF}_2\text{-HbipoPF}_6$ complexes. The scanning electron microscopy (SEM) images show these BF_2 complexes reveal the interesting and various morphological changes upon variation of the solvent type or polarity (Fig. 1). The complex **A-1** ($\text{BF}_2\text{-HbipoPF}_6$, prepared by

using water as a solvent) discloses two-dimensional (2D) rhombic microsheet morphology (Fig. 1a). However, when solvent water was exchanged with acetonitrile by the same solid-phase anion exchange reaction condition, the resultant complex **A-2** (also $\text{BF}_2\text{-HbipoPF}_6$) presents unusual three-dimensional (3D) hexangular prismlike morphology (Fig. 1b). Moreover, when using ethanol and acetone as solvents, the induced **A-3** and **A-4** (also $\text{BF}_2\text{-HbipoPF}_6$) reveal the flower-like morphology composed of 2D microsheets (Fig. 1c), and zero-dimensional (0D) particle-like morphology (Fig. 1d), respectively. The PXRD patterns confirm the microstructures of **A-1–A-4** to be highly crystalline (Fig. S1 in supplementary material). Also, the different PXRD patterns of **A-1–A-4** also indicate their various microstructures. Obviously, different solvents play important roles in controlling the morphologies of organic microstructural materials.

On the other hand, when using various solvents, solid-phase anion exchange reactions between $\text{BF}_2\text{-HbipoCl}$ and SCN^- anion [18] also led to the formation of interesting morphologies of four $\text{BF}_2\text{-HbipoSCN}$ complexes (Fig. 2). The complex **B-1** ($\text{BF}_2\text{-HbipoSCN}$, prepared using water as a solvent) exhibits the 2D rectangle microsheet-like morphology (Fig. 2a). Interestingly, when solvent water was exchanged with acetonitrile or ethanol, the induced **B-2** or **B-3** (also $\text{BF}_2\text{-HbipoSCN}$) presents thicker (Fig. 2b) or longer (Fig. 2c) 2D rectangle microsheet morphology, respectively. Moreover, when using acetone as a solvent, the resultant complex **B-4** (also $\text{BF}_2\text{-HbipoSCN}$) reveals interesting 3D cubelike morphology (Fig. 2d). The PXRD patterns also confirm the microstructures of **B-1–B-4** to be highly crystalline and show different microstructures (Fig. S2 in supplementary material).

Because all microstructural materials were fabricated by the same conditions, the factors of pH and temperature, etc., are not responsible for formation of different morphologies. Instead, solvents have a profound effect on the morphologies of these microstructural materials. The exact mechanism for the solvent-induced morphology is still not clear, but, it is noteworthy that the solvent is the only difference of reaction conditions in assembly of such morphologies, demonstrating the solvent-induced morphological changes [25–31]. Under protic solvent (water and ethanol) conditions, the 2D sheetlike **A-1** (Fig. 1a), **A-3** (Fig. 1c), **B-1** (Fig. 2a) and **B-3** (Fig. 2c) were obtained. We can hypothesize that the solvated PF_6^- (or SCN^-) anions were selectively adsorbed on a specific crystal facet due to the hydrogen bonding interactions between protic solvent and $\text{BF}_2\text{-Hbipo}$ molecule (Fig. 3), resulting in the anisotropic growth to give sheetlike **A-1**, **A-3**, **B-1** and **B-3**. It is noteworthy that weaker polarity of protic ethanol solvent induces less uniform sheetlike morphology of **A-3** (Fig. 1c) and **B-3** (Fig. 2c), and even **A-3** reveals the flower-like morphology composed of 2D microsheets. In other words, stronger polarity of protic water solvent favours a higher symmetry microstructure of **A-1** (Fig. 1a) and **B-1** (Fig. 2a) [32]. Therefore, we can deduce that solvent polarity is likely to be responsible for the different morphologies.

Moreover, under aprotic dipole solvent (acetonitrile and acetone) conditions, 3D hexangular prismlike **A-2** (Fig. 1b), 0D particle-like **A-4** (Fig. 1d), thicker rectangle microsheet of **B-2** (Fig. 2b), and 3D cubelike **B-4** (Fig. 2d) were assembled. Obviously, the protic/aprotic nature of solvents is likely to be responsible for the different observed morphologies (2D microsheets vs. 0D particles, 3D hexangular prisms or cubes) on switching from protic water or ethanol to aprotic acetonitrile or acetone. We hypothesize that PF_6^- (or SCN^-) anion which was solvated by aprotic dipole acetonitrile or acetone, was adsorbed on different crystal facets due to absence of specific hydrogen bonding interactions, giving rise to formation of non-sheetlike morphologies. Moreover, it is found that the polarity of dipole solvents also has an important influence on morphologies. Because acetone solvent with lower polarity only

Download English Version:

<https://daneshyari.com/en/article/7922370>

Download Persian Version:

<https://daneshyari.com/article/7922370>

[Daneshyari.com](https://daneshyari.com)