Time-dependent morphology evolution and density functional theory calculations to study crystal growth process of a triphenylamine nanorod

Lin Kong [a], Jia-Xiang Yang [a], Long-Jiu Cheng [a], Peng Wang [a], Hong-Ping Zhou [a], Jie-Ying Wu [a], Yu-Peng Tian [a,b,c,*], Bao-Kang Jin [a], Xu-Tang Tao [b]

[a] Department of Chemistry, Key Laboratory of Functional Inorganic Materials of Anhui Province, Anhui University, Hefei 230039, PR China
[b] State Key Laboratory of Crystal Materials, Shandong University, Jinan 502100, PR China
[c] The State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, PR China

HIGHLIGHTS

- Crystals of a triphenylamine derivative in micro- and macro- size were investigated.
- Weak interactions between adjacent molecules were computational calculated through DFT method to study the orientation growth.
- The calculation result was helpful to understand the relationship of molecular structure and crystal growth process.

GRAPHICAL ABSTRACT

Crystals in micro- and macro- size of [4-(diphenylamino)phenyl]methylene-propanedinitrile were investigated. Weak interactions between adjacent molecules were computational calculated through time-dependent density functional theory to understand the relationship between molecular structure and crystal growth process.
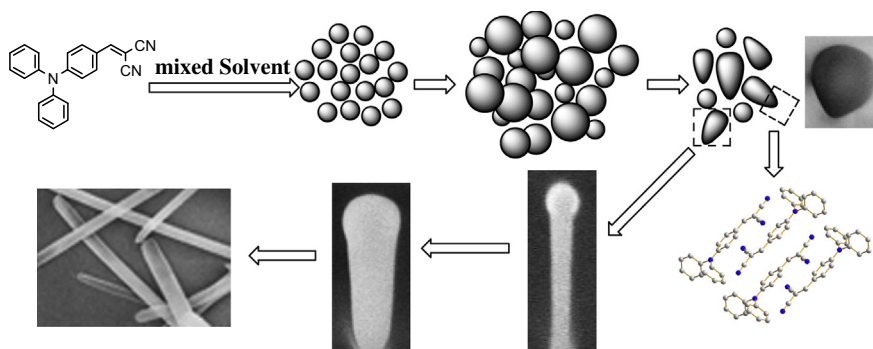
ABSTRACT

In this study, a typical intramolecular charge transfer (ICT) triphenylamine derivative, [4-(diphenyl-amino)phenyl]methylenepropanedinitrile (abbreviated as **DPMP**) was synthesized. Controllable one dimensional (1D) nanocrystals of **DPMP** have been obtained through reprecipitation method. The thermodynamic relationship of the molecular structure and growth process in nanometer scale of **DPMP** was investigated through density functional theory (DFT) calculation, which was performed on the weak interactions between adjacent molecules. The results showed that the assembling interactions along *a* axis were much stronger than that along *b* and *c* axis, which meant that 1D orientation growth along *a* axis would be the most stable state in thermodynamics, that is to say, **DPMP** molecules tended to form 1D orientation structure. The study is helpful to understand the relationship of molecular structure, weak interactions, orientation growth process and self-assembling morphology.

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1. Introduction

In the past few years, nanomaterials based on functional organic molecules attracted considerable attention. Such organic nanomaterials possessed unique optical and electronic properties [1], which would lead to potential applications in various fields

* Corresponding author at: Department of Chemistry, Key Laboratory of Functional Inorganic Materials of Anhui Province, Anhui University, Hefei 230039, PR China. Tel.: +86 551 63861279.
 E-mail address: yptian@ahu.edu.cn (Y.-P. Tian).

[2], such as color-tunable display [3], electrochemical sensors [4], light-emitting diodes [5], field-effect transistors [6], solar cells [7], optical waveguides [8] and so on. Generally, the growth orientation of organic nanostructures was very important to their properties [9]. Wang group [10] reported that the evolution of tetracyanoquinodimethane (TCNQ) structures from netted 1-D microbelts to flowerlike supernanostructures led to dramatic enhancements of explosive detection speed. Zhu group [11] carefully investigated the relationship between morphology (1-D, 2-D and/or 3-D) and mobility of a group of terphenyl derivatives.

The driving forces, which constructed the orientation assembly of organic nanomaterials, played very important role in the nature of the materials and their potential applications. The direction of donor–acceptor dipole–dipole attraction between intramolecular charge transfer (ICT) molecules can be used to guide the preferential growth. And the directions of the dipole moments would construct the favored directions of molecular stacking and thus the corresponding morphologies. Both the donor and the acceptor groups are completely aligned in one direction along the D–A and/or D–π–A type molecules. Thus, this type of molecules would aggregate along this direction to form 1-D and/or semi-2-D nanomaterials.

However, self-assembly by weak interaction-directed molecular stacking is also an important factor in constructing organic nanomaterials. Hydrogen bond, π–π stacking, van der Waals contact, etc. are the main driving forces in constructing the organic molecules to nanostructures with defined morphologies [9,12]. Moreover, the self-assembly process of an organic molecule also relies on the induction from the surroundings, such as the interactions between the organic molecule and the solvent or the surfactant. Considering the above several factors as a whole, the intermolecular forces between adjacent molecules played important role in construction of nanomaterials.

As was known, the energy of these weak interactions could be easily calculated by convenient single-point density functional theory (DFT) calculation of energy, the outcome of which could be provided to explain the building-block information [13]. Recently, Lehmann [14] used this method to predict molecular crystal structure through only the structural formula. Our team, focusing on the interaction energy in the supramolecular systems, had also achieved some good results [15], through which we believed that this calculation method could also be applied to investigate the relationship between molecular interactions and the crystal growth of an organic compound.

Considering all the above aspects, in this work, a triphenylamine derivative, [4-(diphenylamino)phenyl]methylene-propanedinitrile (abbreviated as **DPMP**), was designed and prepared, in which triphenylamine group was employed as electron-donor unit, the dicyano group as an electron-acceptor unit, and they were linked by a vinyl bond to form a novel organo-soluble D–π–A type molecule [16]. Thus, the triphenylamine group and vinyl bond afforded π–π stacking interactions and the dicyano group would lead to weak interactions. Moreover, **DPMP** was a typical intramolecular charge-transfer (ICT) compound and had caused many interests. In 2008, Chen et al. [16] reported the synthesis of it. 2009, Li et al. [17] reported the crystal structure of it. Recently, our group studied its optical properties [18]. However, the morphology of **DPMP** nanostructures had not been studied, not to say the relationship between the molecular structure, the weak interactions between adjacent molecules and the crystal growth process. Thus, in this

study, the directional weak interactions between neighboring **DPMP** molecules were calculated through DFT method. The results explained the orientation growth of **DPMP** in both macro and micro size, and fitted the experimental data very well.

2. Experimental section

2.1. Preparation of DPMP

DPMP was synthesized as described in Scheme 1. In detail, 4-diphenyl-aminobenzaldehyde was synthesized in accordance with the reported method [19]. **DPMP** was synthesized from 4-diphenylaminobenzaldehyde and malononitrile *via* solvent-free reaction in 94% yield. FT-IR (KBr, cm^{-1}) selected bands: v = 3049 (v_{CH2}, w), 2216 ($v_{C\equiv N}$, s), 2648 (w), 1446 (m), 1186 (s), 821 (w). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.74 (d, J = 8.8 Hz, 2H), 7.51 (s, 1H), 7.38 (t, J = 8.0 Hz, 4H), 7.25–7.18 (q, 6H), 6.95 (d, J = 9.2 Hz, 2H). ^{13}C NMR (100 MHz) δ = 75.56, 114.08, 118.48, 122.79, 126.12, 126.71, 129.95, 132.98, 145.14, 153.47, 157.89, 166.30. *Anal. Calc.* for C$_{22}$H$_{15}$N$_3$: C, 82.22, H, 4.70, N, 13.08, Found: C, 82.78, H, 4.87, N, 12.74%. MS (EI), m/z (%): 321 ([M$^+$], 100).

Single crystal suitable for structure analysis was obtained by slow evaporation of THF and EtOH mixed solution of **DPMP** at room temperature.

2.2. Preparation of DPMP nanostructures

Stable colloid of **DPMP** was prepared through reprecipitation method [12], which led to highly monodisperse nano and/or submicrocrystals with well-defined morphology. In typical experiments, **DPMP** was dissolved in EtOH (2.0×10^{-3} mol/L). Then, 200 μL of the solution was injected into 5 mL of high-purity water under stirring. After being stirred for 3 min, the sample was left undisturbed for stabilization.

2.3. Characterization

The morphologies were obtained on field-emission scanning electron microscope (FESEM, Hitachi S-4800) and electron microscope (TEM, JEM-2100). The X-ray diffraction measurements were performed on a Bruker SMART CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 298(2) K. Intensity data were collected in the variable ω-scan mode. The structures were solved by direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. Calculations were performed with the SHELXTL-97 program package [20].

2.4. DFT calculation

Calculations were carried out *via* DFT method [21] (Gaussian 09 [22]). We fixed Cartesian coordinates of non-hydrogen atoms, and optimize hydrogen atoms to its most suitable coordinates. Single-point energy calculations at M06/6-31+g(d,p) level basis set were performed to obtain assembling energy between two relative fragments, which was defined as $E_{\text{interaction}} = E_{\text{dimer}} - 2E_{\text{molecule-free}}$. The data were corrected by basis set superposition error (BSSE) [23].

3. Results and discussion

3.1. The morphology of DPMP

At present work, **DPMP** nanostructures were simply prepared in ethanol solution with no addition of any surfactant, template or catalyst. Examination of FESEM and TEM showed that **DPMP**
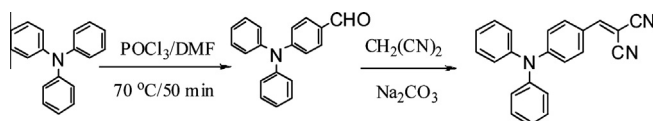
Scheme 1. The synthetic routes for **DPMP**.