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

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# 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.

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#### G R A P H I C A L A B S T R A C T

Crystals in micro- and macro- size of [4-(diphenylamino)phenyl]methylene-propanedinitrile were investigated. Weak interactions between adjacent molecules were computational calculated through timedependent 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-(diphenylamino)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



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[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- $\pi$ -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,  $\pi$ - $\pi$  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 $-\pi$ -A type molecule [16]. Thus, the triphenylamine group and vinyl bond afforded  $\pi$ – $\pi$ 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



Scheme 1. The synthetic routes for DPMP.

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<sup>-1</sup>) selected bands:  $v = 3049 (v_{CH2}, w)$ , 2216 ( $v_{C=N}$ , s), 2648 (w), 1446 (m), 1186 (s), 821 (w). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (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). <sup>13</sup>C NMR (100 MHz)  $\delta = 75.56$ , 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<sub>22</sub>H<sub>15</sub>N<sub>3</sub>: 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<sup>+</sup>], 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 ( $2.0 \times 10^{-3}$  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 K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 298(2) K. Intensity data were collected in the variable  $\omega$ -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. Singlepoint 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  $E_{interaction} = E_{dimer} - 2E_{molecule-free}$ . 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** 



Fig. 1. (a) SEM image of DPMP (Insert: typical SEM image with open-ended structure). (b) TEM image of DPMP. (c) HRTEM image of an individual DPMP rod.

tended to form submicrorod (that is to say 1-D structure) under this condition with diameter and length of about hundreds of nanometers and tens of micrometers, respectively (Fig. 1a and b). Some of the rods also exhibited tube structure as typically shown in Fig. 1a. The high resolution transmission electron microscopy (HRTEM) image (Fig. 1c) showed that the rods had single crystalline structure, which was further supported by X-ray diffraction (XRD) patterns as shown in Supplementary material Fig. S1.

#### 3.2. The morphology evolution study

The nanocrystal growth was further monitored over time at room temperature to investigate the formation process of the as-prepared 1-D structure. Time-dependent morphology evolution experiments were performed by intercepting intermediate products in different reaction stages of 10, 40, 70, and 100 min. Fig. 2 clearly showed the evolution process of DPMP crystals by varying the reaction time. In the initial 10 min, nearly monodisperse nanoparticles formed. with the diameter of about 150 nm (Fig. 2a). As growth time proceeded, the nanoparticles grew larger, with the diameter substantially increased to about 260 nm (Fig. 2b). Very rough surface suggested that the particles could be not stable and may start to transfer into other phases. When stabilizing time was further prolonged to 70 min, the existence of peach-like intermediates was observed as shown in Fig. 2c (typically marked with an arrow). These peach-like intermediates were considered as the gem of the wirelike products. It was believed that the traditional solution-liquidsolid (SLS) process controled the growth [24]. When the growth time extended over 100 min, a large number of nanorods formed. At the same time, it was also noted that the foregoing peach-like intermediates disappeared (Fig. 2d). As time was prolonged to 4 h, the etching effect [12] of EtOH reacted on the morphology, thus, nanotubes appeared (Fig. 1a). Overall, the morphology and size of the structure varied significantly in the early time. Then the change tended stable after nanorods formed, with the length of the rod continuing to increase, till the etching effect influenced the morphology.

#### 3.3. Crystal structure of DPMP

To gain insight into the molecular organization of 1-D architecture, single crystal of **DPMP** was analyzed at room temperature.

X-ray crystallography analysis indicated that **DPMP** molecule existed in the monoclinic space group P2(1)/c with a = 7.01(9) Å, b = 15.89(2) Å, c = 16.09(2) Å and  $\beta = 95.07(2)^{\circ}$ . Crystallographic crystal data and processing parameters for **DPMP** were shown in Table S1. Selected bond lengths and bond angles were listed in Table S2. In the molecular structure of **DPMP** (Fig. 3a), the sum of three C-N-C angles taking nitrogen atom as center was 359.9° (C(7)-N(1)-C(12), 121.6(2)°, C(7)-N(1)-C(13), 120.8(2)° and C(12)–N(1)–C(13), 117.5(2)°). Therefore, the N(1) atom and three adjacent C atoms were approximately coplanar. The bond lengths of N(1)–C(13) (1.439(3)Å) and N(1)–C(12) (1.429(3)Å) were longer than that of N(1)–C(7) (1.373(3)Å), confirming two electrons on N(1) were partial to the adjacent phenyl ring. All the bond lengths of C–C were located between the normal C=C double bond (1.34 Å) and C–C single bond (1.54 Å), especially the bond between C(2) and C(9) (1.429(4)Å), C(2) and C(10) (1.424(4)Å), C(1) and C(3) (1.429(3)Å). It was clearly shown in Fig. 3a that C2, C3, C9, C10, N2 and N3 were in the same plane approximately (in fact, the maximum atomic distance to the corresponding molecular plane was only 0.0055 Å), with the dihedral angles between this plane and the corresponding phenyl ring linked to them being 7.4° (C1, C5–C8, C11), that is to say, the two cyanic radicals, C=C double bond, and the related phenyl ring were at the same plane approximately, which contributed to the extend of the conjugated system.

The structure data of **DPMP** were similar to that reported in Ref. [17]. The main difference was in the torsion of the phenyl rings. In Ref. [17], the dihedral angles between the three phenyl rings were 70.05(1)°, 72.667(3)° and 74.16(3)°, respectively. While they were 72.24(9)°, 72.36(8)° and 74.84(8)°, respectively in this work. Furthermore, Li et al. [17] got organe, irregular shaped crystals form hexane. While it was red, needle crystals for **DPMD** crystalized out of THF/EtOH mixed solution. In the case of this point, the different polarity of the solvents was the main cause. Hexance was a low polarity solvent while ethanol or THF was polar. It was well known that the morphology of a crystal was extremely depended on the crystallization solvents.

The intermolecular interactions of **DPMP** were very similar to that reported in Ref. [17]. The adjacent molecules of **DPMP** were stacked through multiple weak C—H···N weak interactions and  $\pi$ - $\pi$  stacking interactions as shown in Fig. 3b–d. Weak interaction



Fig. 2. Morphologies of DPMP at different stabilizing time from EtOH/H<sub>2</sub>O mixed solution: (a) 10, (b) 40, (c) 70 and (d) 100 min.



**Fig. 3.** (a) Molecular structure and atom numbering of **DPMP**. (b) 1-D framework along *b* axis showing C15–H15…N3 weak interactions (purple) at a distance of 2.967 Å. (c) 1-D framework along *c* axis showing C18–H18…N2 weak interactions (orange) at a distance of 2.874 Å. (d) 1-D framework along *a* axis showing C–H…N weak interactions (green and red) and  $\pi \dots \pi$  interactions (yellow). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

parameters were listed in Table S3. The molecules were connected through C15-H15...N3 weak interactions to form 1-D framework along b axis (Fig. 3b) with H15...N3 distance of 2.967 Å and the angle of C-H···N being 142.4°. DPMP molecules were also connected through C18-H18...N2 weak interactions to form 1-D framework along c axis (H18···N2 distance of 2.874 Å and C–H···N = 132.6°, Fig. 3c). Above all, the type of interactions along a axis were more than that along the other two. Along *a* axis, C20–H20...N2 hydrogen bonds (H20...N2 distance of 2.596 Å, which was slightly shorter than the sum of van der Waals radii [25] of H and N atom,  $C-H \cdots N = 158.6^{\circ}$ ) and  $C17-H17 \cdots N2$  weak interactions (H17···N2 distance of 2.688 Å, C–H···N = 150.5°) existed to stack DPMP molecules into 1-D framework. In this work, all the distances of  $C \cdots N$  were shorter than the corresponding  $C \cdots N$  distance found in documents reported by Thalladi et al. [26] and Zhou et al. [15]. There also existed moderately strong  $\pi$ - $\pi$  intermolecular interaction along a axis with a shortest separation of ca. 3.458 Å (Fig. 3d). The stacking distance was proved from HRTEM analysis (Fig. 1c), which showed the distinct lattice spacing of ca. 0.35 nm corresponding to (200) planes calculated by formula (1) for monoclinic system,

$$d^{2} = \frac{a^{2}(1 - 3\cos^{2}\alpha + 2\cos^{3}\alpha)}{(h^{2} + k^{2} + l^{2})\sin^{2}\alpha + 2(hk + kl + hl)(\cos^{2}\alpha - \cos\alpha)}$$
(1)



**Fig. 4.** Schematic representation of the mode for the growth of nanorod: (a) the nucleation process when **DPMP** solution was mixed to a poor solubility environment; (b) metastable aggregates; (c–h) crystal growth process along 1-D direction; and (i) molecule stacking.

where *a* was the cell length and  $\alpha$  was the cell angle. The results suggested that the as-prepared submicrorods were single-crystalline with the preferential growth along [100] orientation, that is to say, along *a* axis.

Based on the observations and analysis mentioned above, the formation process of **DPMP** nanostructure underwent three main stages, which was schematically proposed in Fig. 4. First, supersaturation of **DPMP** in the mixed solvent led to precipitation of **DPMP** molecule to form nuclei and some metastable aggregated (Fig. 4a and b). Here, the liquid–liquid interface was unique alternative platform for spatially separating both the nucleation and growth of nanocrystals. Then, the traditional SLS process controled the growth, then 1-D orientation growth gradually appeared and nuclei grew preferentially along *a* axis (Fig. 4c–h). Once crystal growth began, continual of molecule orientation growth along the preferred direction would form 1-D structure. The whole formation process of rod took place at identical reaction conditions, and thus one can easily fabricate different morphologies of **DPMP** *via* the present solution route at specific time.



**Fig. 5.** Morphologies of **DPMP** from different solvents: (a) N,N-dimethyl formamide (DMF), (b) benzene, (c) tetrahydrofuran (THF), and (d) ethylene glycol (EG).



**Fig. 6.** Fragments selected for weak interactions along: (a) *a* axis, (b) *b* axis, and (c) *c* axis.

#### Table 1

Total, assembling energies of DPMP and perylene molecules along different directions at M06/6-31+g(d,p) level.

Orientation	Energy (Hatree)		Binding energy $\Delta E$ (kJ/mol)
	(dimer)	(molecule-free)	$\Delta E^{a}$
001 010	-2021.08459 -2021.07988	-1010.53946	-14.87 -2.51
100	-2021.10317		-63.67

 $\Delta E^{a} = E_{dimer} - 2E_{molecule-free}$ ;  $\Delta E^{b} = E_{tetramer} - 2E_{dimer}$ .

#### 3.4. Effect of solvent on the aggregation

As was discussed above, the crystallization solvents affected the morphology of a crystal in macro size very obviously. In this part, the influence of solvent on the aggregation in micro size was studied. Solvents with different polarity were chosen, such as benzene, THF, DMF and EG. The slovent-induced morphological change of **DPMP** is remarkable. The typical SEM images were shown in Fig. 5. Nanodots were obtained from benzene (Fig. 5b), which clearly showed 1-D aggregation tendency to form fractal geometry morphology. The as-fabricated DPMP nanostructures from THF (Fig. 5c) revealed nanorods with tens of nanometers width, and hundreds of nanometers length, while products from EG formed nanobeam compositing of nanorods (Fig. 5d), aggregation of nanorods were observed from DMF (Fig. 5a). The phenomena can be attributed to different intensity of noncovalent intermolecular interactions between **DPMP-DPMP** and **DPMP**-solvents [12,27]. The solvent affect on morphology in either macro or micro size was consistent.

## 3.5. DFT calculation

To explain molecular level causes of orientation growth, weak interactions between adjacent molecules were computational calculated by varying the intermolecular position and different packing models along a, b and c axis (Fig. 6). The selected fragments were cut out directly from the CIF data. During the calculating procedure, the basis set superposition error (BSSE) can have a strong effect on the calculated geometries and interaction energies, especially if the calculations are carried out within relatively small basis sets such as 6-31+g(d,p). Thus, for the geometry corresponding to the lowest energy at this M06/6-31+g(d,p) level, we then performed counterpoise correction calculations, to obtain estimates of the basis set superposition error (BSSE) at the M06 levels, which gives our best estimates of the weak interaction strength. The total energy and molecule–molecule assembling energy were listed in Table 1.

The results showed that the dimers from different directions were lower in energy than two times of that of free molecule. The calculated assembling energy along *a* axis was -63.67 kJ/

mol, which was much lower than that along *b* and *c* axis (-2.51 and -14.87 kJ/mol, respectively). The result indicated that the interactions along *a* axis were much stronger than that from the other two, which would lead to 1-D orientation growth along *a* axis in nature. The result was consistent with X-ray crystallography and nanocrystal analysis (Fig. S1). Such effects provided a basis to explain the orientation growth of **DPMP**, and might be helpful to understand the relationship of molecular structure and self-assembling morphology.

# 4. Conclusion

In summary, a triphenylamine derivative **DPMP** was synthesized by solvent-free reaction with high yield. Controllable 1-D nanocrystals with single crystalline structure were obtained through reprecipitation method. The formation process of the asprepared 1-D structure was studied *via* time-dependent morphology evolution experiments. Weak interactions between adjacent molecules were computational calculated through DFT method to gain insight into the orientation growth. The result indicated that the interaction along *a* axis was the strongest which would lead to 1-D orientation growth along *a* axis in nature. The result is helpful to understand the relationship of molecular structure, weak interactions, orientation growth process and self-assembling morphology.

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#### **Appendix A. Supplementary material**

Crystallographic data reported in this manuscript were deposited with Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-698910. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (+44) 1223-336-033, or email: deposit@ccdc.cam.ac.uk.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013.11.017. These data include MOL files and InChiKeys of the most important compounds described in this article.

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