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.

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.

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ABSTRACT

In this study, a typical intramolecular charge transfer (ICT) triphenylamine derivative, [4-(diphenylamino)phenyl]methylene-propanedinitrile (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.
[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 properties [9]. Wang group [10] reported that the evolution of organic nanostructures was very important to their properties.

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 intramolecular 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: ν = 3049 (υCH₂, w), 2216 (υC≡N, s), 2648 (w), 1446 (m), 1186 (s), 821 (w). ¹H NMR (400 MHz, CDCl₃) 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), 13C 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. 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 precipitation method [12], which led to highly monodisperse nano and/or sub-microcrystals with well-defined morphology. In typical experiments, DPMP was dissolved in EtOH (2.0 × 10⁻² 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 θ-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(dp) level basis set were performed to obtain assembling energy between two relative fragments, which was defined as Einteraction = Edimer − 2Emolecule-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...
X-ray crystallography analysis indicated that DPMP molecule existed in the monoclinic space group P2(1)/c with \( a = 7.01(9) \text{ Å}, b = 15.89(2) \text{ Å}, c = 16.09(2) \text{ Å} \) 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)°, 72.56(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 organically 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. Hexane 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.
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⋯N = 158.6°) and C17−H17⋯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⋯N were shorter than the corresponding C⋯N distance found in documents reported by Thalladi et al.[26] and Zhou et al.[15]. There also existed moderately strong π−π 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,

\[
\frac{d^2}{2} = \frac{a^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)}{2(hk + kl + hl)(\cos^2 \alpha - \cos^2 \beta)}
\]

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. 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 π−π interactions (yellow). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**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.

**Fig. 5.** Morphologies of DPMP from different solvents: (a) N,N-dimethyl formamide (DMF), (b) benzene, (c) tetrahydrofuran (THF), and (d) ethylene glycol (EG).
The solvent affect on morphology in either macro or micro size DPMP interactions between attributed to different intensity of noncovalent intermolecular 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.

### 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 solvent-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 $-63.67 \text{kJ/mol}$, which was much lower than that along b and c axis ($-2.51$ and $-14.87 \text{kJ/mol}$, 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.

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### 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 as-prepared 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/contents/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.

### References
