

Isomeric Effect on Microscale Self-Assembly: Interplay between Molecular Property and Solvent Polarity in the Formation of 1D *n*-Type Microbelts

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Isomerism, a well-known phenomenon, results from the difference in atomic connectivity for molecules having the same chemical formula.^[1] Isomers with the same main carbon skeleton which differ in the position of functional groups may have drastically different physical and chemical properties. In nature, for example, the mere change of the position of a methyl group might modify the biological activity of the whole protein. In one case, the *EcoRV* restriction endonuclease changes its selectivity towards Mg²⁺ as the cofactor to Mn²⁺, after an isoleucine unit near the active site was replaced by leucine.^[2] However, how such isomeric effects are expressed at the nano- and microscale, and in device performance, remains an interesting yet seldom explored question.

One-dimensional (1D) nano- or microstructures based on organic semiconductors have attracted much attention due to their potential application in photoelectronic devices such as transistors, light-emitting diodes, and photovoltaic cells.^[3] Among all noncovalent interactions, π - π stacking is considered as one of the main driving forces for the formation of 1D assembly.^[4] By modulating the size of the conjugated planes, the type and the length of the substituents, or the external conditions such as temperature, different morphologies including wires and tubes were achieved.^[5] However, little has been done to explore the effect of the position of substitution at the conjugated core on the formation of the

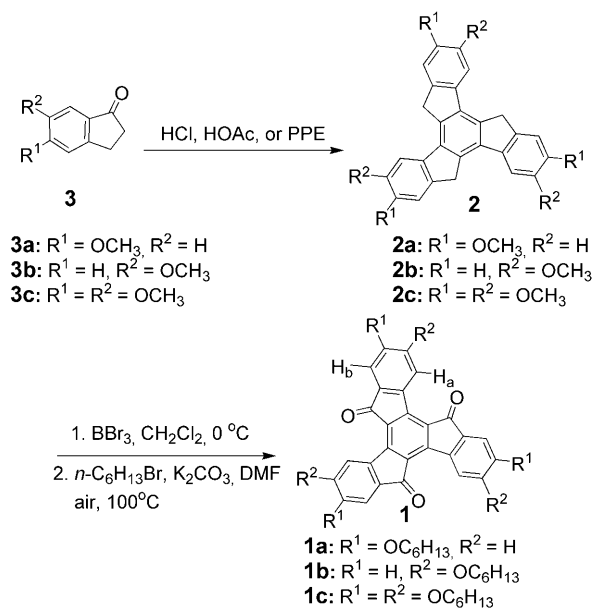
1D microstructure, which would not only lead to a new dimension in molecular design but also help us to gain further insight into the self-assembly process. Herein, we report the development of a family of *n*-type semiconductors under mild conditions, and their different self-assembly behavior in various solvents. We observed an interesting “isomeric effect” at microscale, which is explained by detailed calculation, and with which we have been able to set some general rules regarding the one-dimensional self-assembly process of planar π -conjugated molecules.

n-Type organic semiconductors are indispensable for diodes and complementary circuits with high operation speed and low power consumption, but their development lags far behind that of their *p*-type counterpart.^[6] As part of our continuing efforts toward synthesizing new organic *n*-type materials, we have identified truxenone as a promising candidate. The three carbonyl groups of truxenone greatly reduce the electron density of the aromatic core, a feature that has been shown to effectively promote π - π interaction,^[7] which is important for the conduction of electrons in *n*-type materials. Compounds **1a–c** were synthesized from **2a–c** in one step by combining oxidation and alkylation. The electron-deficient aromatic core of truxenone and its C₃ symmetry provide us with an excellent platform to investigate the delicate interplay between the molecular properties and solvent polarities in the self-assembly of 1D microstructures. We found that the effect of substitution at different positions and the number of substituents are reflected not only at the molecular level, but also in the different behavior observed during the formation of the 1D microstructures. Such an understanding would contribute much to the future molecular design of self-assembly processes. In addition, the obtained microstructures, which display a large aspect ratio, are ideal for the construction of FET devices.^[8]

Scheme 1 illustrates the synthetic approach to truxenone derivatives **1a–c**. The trimerization of **3a–c** catalyzed by acid afforded **2a–c**. After demethylation of **2a–c** by BBr₃ in CH₂Cl₂, reaction with *n*-hexyl bromide in a suspension of K₂CO₃ and DMF in air afforded **1a–c**. In our newly devel-

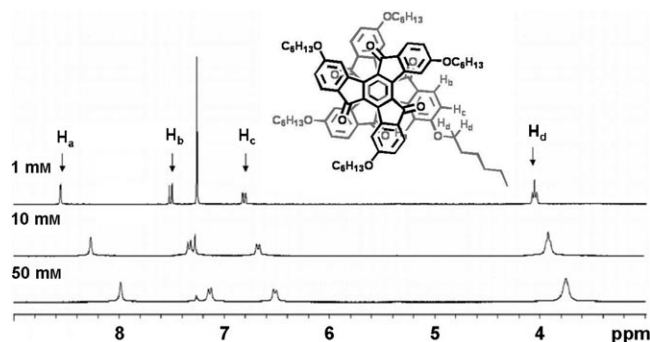
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Scheme 1. The synthetic approach to **1a–c**.

oped method, alkylation and oxidation were accomplished in one step under mild conditions and in good yield, in sharp contrast to the harsh conditions and low yield usually employed in the construction of the truxenone core.^[9] The mechanism of the one-step reaction might be similar to that in the facile oxidation of a fluorene unit, namely involving the generation of carbonanion.^[10] Indeed, in protic solvents such as ethanol, only the corresponding nonoxidized compounds were obtained. The identity and purity of all as-synthesized compounds were confirmed by ^1H NMR and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis (see the Supporting Information).

The self-assembly behavior of such a planar conjugated system through π – π stacking was first characterized by concentration-dependent ^1H NMR spectra. For example, for **1b**, the signal at $\delta = 8.56$ ppm, which was assigned to proton H_a , significantly shifted upfield to $\delta = 7.99$ ppm as its concentration in CDCl_3 increased from 1 mM to 50 mM at room temperature (Figure 1). Another two signals assigned to protons H_b and H_c showed similar upfield shifts. Such shifts are a result of shielding from the ring current of neighboring aromatic molecules by cofacial stacking.^[11] The signal at $\delta = 4.06$ ppm, which corresponds to a methylene group of *n*-hexyloxy, moved to $\delta = 3.75$ ppm. The overall results from the concentration-dependent ^1H NMR spectra indicate that these planar conjugated compounds have the potential to form 1D nano- or microstructures through π – π stacking. We tentatively propose the stacking mode to be as shown in Figure 1, which corresponds well with the different extent of chemical shift changes of different protons. Unlike the usually observed slipped cofacial stacking mode, the truxenone cores could rotate relative to each other around the C_3 axis to minimize the electron repulsion between the π electrons,^[12] thanks to the one-directional circular arrangement

Figure 1. Partial ^1H NMR spectra (CDCl_3) of **1b** as the concentration increased from 1 mM to 50 mM.

of the molecular structure. Also, strong local dipoles created by the three carbonyl groups allow the core to stack in a electronically favorable manner.^[13] Finally, due to the stronger π – π interaction between the electron-deficient conjugated planes,^[7b] a strong tendency to self-assemble could be achieved with relatively small cores compared to larger electron-rich polycyclic aromatic hydrocarbons (PAHs). Compound **1c** also showed similar concentration-dependent behavior in the ^1H NMR spectra, although to a smaller extent. During the process, we were surprised to find that the solubility of **1a**, the constitutional isomer of **1b**, was so poor that the same experiment could not be carried out on **1a**, which drew our attention to the large differences in the molecular properties of this pair of isomers.

The differential scanning calorimetry (DSC) of **1a** in nitrogen showed a distinct melting point at around 179°C , well below the decomposition temperature (T_d) at 400°C . Compound **1b** exhibited a distinct glass transition temperature (T_g) at around 95°C and a melting transition (T_m) at 128°C . No T_g and T_m above 50°C were observed for **1c** before its T_d at around 390°C . Such a large difference in melting points further supports our hypothesis that the intermolecular interaction of **1a** and **1b** differ greatly. Therefore, exploring the respective behavior of these two isomers in forming 1D structures should be highly interesting. At the same time, **1c** was also included in the experiment to study the effect of the number of substituents.

The SEM images of the 1D microstructures for **1a**, **1b**, and **1c** in THF, dioxane, and *n*-hexane are shown in Figure 2. As expected, the responses of **1a–c** to these solvents differ greatly as a function of the solvent polarity; however, there are some general trends. After heating in THF at a concentration of 1 mg mL^{-1} , and then cooling down to room temperature, only **1a** formed 1D microbelts (width: $2\text{--}10\text{ }\mu\text{m}$, length: $20\text{--}200\text{ }\mu\text{m}$); **1b** and **1c** did not show any 1D structures under the same conditions. Upon changing to the moderately polar solvent dioxane, microbelts of **1a** with a similar width and length distribution to those observed with THF were obtained. In addition, uniform microbelts of **1b** with a diameter of $1\text{--}2\text{ }\mu\text{m}$ clearly emerged, and microfibers of several hundreds of micrometers in length were readily formed from **1c** in dioxane.

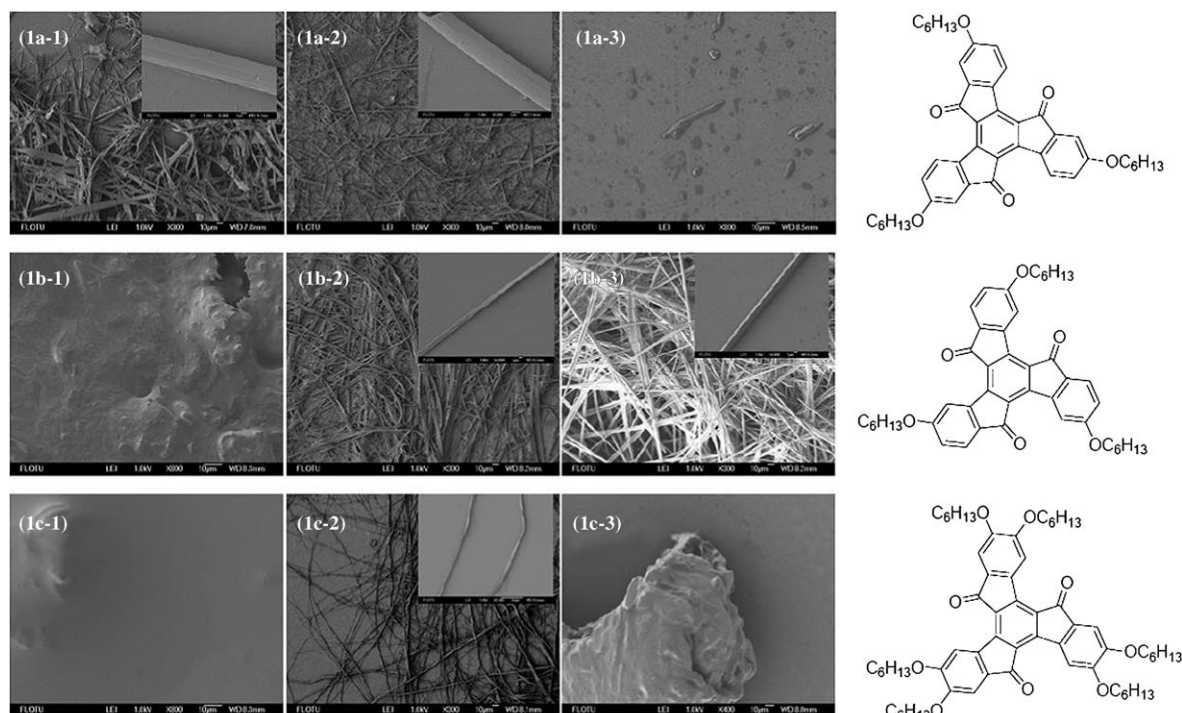


Figure 2. SEM images of **1a–c** precipitate from 1: THF; 2: dioxane; 3: *n*-hexane. Scale bars: 10 μm .

Upon further decreasing the solvent polarity, for example, to *n*-hexane, no assembly structure of **1a** was observed due to its poor solubility. In contrast, microbelts of **1b** not only grew longer but also tended to be more rigid and straight, and irregular structures for **1c** were again observed in *n*-hexane.

To understand the different behaviors of **1a–c**, we performed extensive calculations on their molecular properties. Geometry optimizations and frequency analysis were carried out on **1a–c** with the AM1 method by using the Gaussian03 program package.^[14] The optimized structures are shown in Figure 3. The molecular properties were evaluated by using the B3LYP functional with a 6-31 g(d) basis set. Table 1 lists the calculated total molecular polarizability and molecular electric moments of **1a–c**.

For **1c**, the steric repulsion between the two adjacent side chains forces the alkoxy chains to flip out of the molecular plane in the equilibrium geometry. As a result, **1c** has a dipole moment of 1.99 D, whereas **1a** and **1b** are nonpolar due to their C_{3h} symmetry and nearly planar structures. This significant difference increases the solubility of **1c** in polar solvents such as THF. Moreover, the additional three hexyloxy chains increase van der Waals interaction between **1c** and hexane molecules, which hamper the growth of the 1D structure of **1c** in hexane. Thus, microfibers from **1c** were obtained only in dioxane, a moderately polar solvent with the lowest solvent–solute interaction. From this observation, we suggest that adjacent alkoxy groups might not be a good choice for designing 1D self-assembly structures, unless the

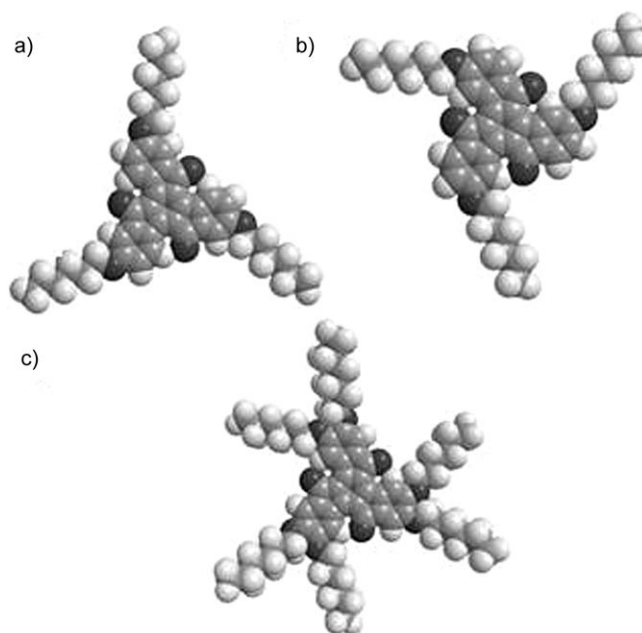


Figure 3. Optimized conformations of a) **1a**; b) **1b**; c) **1c**.

interaction between the aromatic cores is indeed fairly strong.^[15]

The origin of different properties of two isomers **1a** and **1b**, which is highly similar in structure and size, was more subtle. We speculate that the difference might result from the different strength of the π – π interaction along the

Table 1. Dipole moment (μ , Debye), traceless quadrupole moment (Θ , Debye Å), and polarizability (α , au) of **1a–c** at the equilibrium geometry.^[a]

Compd	μ	Θ_{zz}	α
1a	0.00	−23.6	618
1b	0.00	−14.1	591
1c	1.99	−21.1	866

[a] The *z* axis was chosen to coincide with the C_3 axis, thus, $\Theta_{zz} = -2\Theta_{xx} = -2\Theta_{yy}$. For detailed information about the coordinates see Supporting Information.

growth direction of the 1D assemblies. Generally, the interaction between the arene planes can be divided into electrostatic and dispersion interactions.^[7b] Our calculations show that the polarizability, which is correlated with the dispersion interaction,^[16] does not differ greatly for **1a** and **1b**. Hence, it can be inferred that the different performance of **1a** and **1b** is due to their different electrostatic properties. Since these two compounds are both nonpolar molecules, the first nonvanishing electrical moment, traceless quadrupole moment, was used as a description of the molecular charge distribution and the electrostatic interaction between a pair of molecules.^[17] As shown in Table 1, the traceless quadrupole moment as defined by Buckingham^[18] of **1a** is about 50 % larger than that of **1b**, which means that the electrostatic interaction in stacked complexes of **1a** will be much stronger than that in **1b**. To break the relatively strong solute–solute interaction in **1a**, a relatively polar solvent such as THF should be employed to provide suitable solubility for initiating the one-dimensional self-assembly process. In the case of **1b**, the intermolecular interaction between the conjugated cores is much weaker. Therefore, instead of considering the solubility problem, the successful 1D assembly of **1b** requires less interference from solvent molecules. Accordingly, the longest and most uniform 1D structure for **1b** emerges in *n*-hexane, the least polar solvent. The difference in the π – π interaction of **1a** and **1b** also correlates well with other observed properties of **1a** and **1b**, such as their melting points. To sum up, the seemingly small difference in the position of the substituents in **1a** and **1b** drastically changes the molecular properties, which is manifested in their different behavior in forming 1D microbelts. Moreover, from these results, we deduced a semiempirical rule, “like attracts like,” which stresses the importance of the matching between the molecular property and the solvent polarity. We believe that the deduced rules are also applicable to other self-assembly systems.

The HOMO and LUMO energy levels of **1a–c** in thin films were measured by cyclic voltammetry, and calculated from the onset of oxidation and reduction waves, which were −6.20 and −3.09 eV for **1a**, −6.23 and −3.32 eV for **1b**, and −5.97 and −3.06 eV for **1c**, respectively. Their LUMO energy levels, combined with their favorable morphology, indicated that **1a–c** might be promising candidates for *n*-channel FET devices.^[19] Fabrication of devices using the 1D microbelts is in progress in our laboratory.

In summary, we have developed a mild and efficient synthetic approach to truxenone derivatives **1a–c** and investigated their self-assembly behavior in various solvents. This investigation reveals that **1a–c** favor the formation of bulk quantity 1D microstructures through self-assembly under appropriate conditions. The difference in their self-assembly behavior, such as different morphologies and response towards solvent polarity, is rooted in their molecular properties. The computational study reveals some guidelines for designing molecular structures and choosing assembly conditions for future work. Finally, long microstructures are readily obtained from *n*-type semiconductors **1a–c**, which show great potential in integrated nano- or microelectronic devices.

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