論文の内容の要旨

論文題目　Self-Assembly of Propeller-Shaped Triphenylamine Derivatives

（プロペラ構造を有するトリフェニルアミンの自己組織化）

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Molecular self-assembly emerges as a result of the connection of small building blocks through non-covalent linkages, such as hydrogen bonding, electrostatic interaction, or π-π interaction. By the dynamic nature of non-covalent interaction, it is allowed that self-assembled object formed ordered structures upon a spontaneous organization between monomer and aggregated states. These spatial and temporal controllability has attracted interest from material scientists in order to create novel organic materials and devices which have more sophisticated orientations and properties.

In last few decades, the development of supramolecular self-assembly has been mostly focused on the assembly of planar and disk-shaped molecules, such as hexabenzocoronene, benzene tricarboxamide, porphyrin and perylene bisimide, which probably enforce strong molecular stacking. However, non-planar π-conjugated aromatics were rarely utilized, while they displayed unique properties and functions derived from their characteristic structures. For example, low symmetric order of non-planar molecules endows their assemblies with unique features such as macroscopic polarization and chain-growth supramolecular polymerization.

Triphenylamine (TPA) is one of a famous non-planar aromatic molecules that has three-bladed propeller structure and the benzene blades make conrotatory angles of ~ 44° with respect to the plane of central NCCC atoms in a crystal phase. Based on the propeller structure, TPA is expected to give an intrigued motif for the control of molecular orientation and supramolecular chirality. However, the self-assembly of TPA and their correlated property have been rarely studied either in liquid crystalline (LC) state or in the diluted solution. I have investigated the propeller-like TPA derivatives that displayed the unprecedentedly high amplification of supramolecular chirality and hexagonal columnar LC mesophases with electric field responsiveness (Figure 1). Moreover, the spatial effect of linear alkyls and branched chiral chains was investigated by comparing the self-assembly behavior of TPA derivatives, which was dependent on systemically structural variation.

My molecular design was based on the propeller-shaped TPA core and the peripheral paraffinic wedges at *para*-position via amide linkages, which expected to form hydrogen bonding in the assembly (Figure 2). To elucidate the spatial effect of side chains, the alkoxy group in outer phenyls were modified on the basis of three structural variation; 1) the lack of long linear alkyls (**A$_{12}$**, **A$_{-p}$** and **A$_{-m}$**), 2) the existence of branched chiral chains [**C$_{1m}$(*S*)**, **C$_{1p}$(*S*)**, **C$_{2m,m}$(*S*)**, **C$_3$(*S*)**]. These TPA derivatives were synthesized by amide coupling with tris-(4-aminophenyl)amine and various 3,4,5-substituted benzoic acid chloride. The individual paraffinic side chain was produced according to the methods reported by Würthner and co-workers with minor modifications.

In cyclohexane, enantiomeric pure **C$_3$(*S*)** and **C$_3$(*R*)** were exhibited characteristic mirror-image circular dichroism (CD) spectra at a concentration of 3.0×10^{-5} M, which indicating the formation of one-handed helices (Figure 4a). In addition, a density functional theory (DFT) computational study suggested that central aromatics also adopted a propeller shape in the assembly (Figure 3a). By monitoring vibrational circular dichroism (VCD) spectra, I could successfully confirm the propeller chirality of central aromatics as well as the helical alignment of amide units in the helical assemblies (Figure 3b). In the spectral range from 1660 cm^{-1} to 1550 cm^{-1}, two strong bands corresponded to a stretching vibration of C=O bonds in helical array of amide groups through hydrogen bonds. Moreover, a clear Cotton effect was observed at 1550 ~ 1500 cm^{-1} corresponding the chiral conformation of central aromatics.

In supramolecular aggregates, by mixing achiral molecules with small fraction of chiral additives, the chiral amplification was exhibited through efficient transfer of chirality intermolecularly and called as the sergeants and soldiers principle. To confirm the effect of aromatic propellers for efficient chiral transfer, the sergeants and soldiers experiment was performed to co-assembled mixtures of chiral sergeant, **C$_3$(*S*)**, and its achiral analogue, **A$_{12}$**, in cyclohexane. As expected, the nonlinear increment of CD intensity was observed with increasing the fraction of **C$_3$(*S*)** in the cyclohexane solution of **A$_{12}$** and the saturation of CD intensity was found even at the 0.3 % of **C$_3$(*S*)** (Figure 4a,b). It is the best record that the helicity of supramolecular polymers was fully biased to one-handed helicity compared to the previous record with only 1% of sergeants. In addition, the biased propeller conformation of achiral soldiers in the co-assembled mixture was confirmed by the mirror-image of VCD spectra, which was an identical waveform with those of pure chiral sergeants (Figure 3b,c).

Although **C$_3$(*S*)** emerged the strong chiral sergeant ever, I further investigated the chiral amplification of another chiral analogues, **C$_{1m}$(*S*)**, **C$_{1p}$(*S*)** and **C$_{2m,m}$(*S*)**, which were reduced the number of stereogenic centers presented in a molecule. Intriguingly, **C$_{1p}$(*S*)** exhibited the weak chiral amplification while the **C$_{1m}$(*S*)** and **C$_{2m,m}$(*S*)** induced strongly helical biases in supramolecular fibers, like as **C$_3$(*S*)** (Figure 4b). It revealed that the *meta*-position of outer phenyls played a critical role in the process of chiral amplification.

To elucidate the spatial effect of side chains at *meta*-position of paraffinic wedges, the self-assembly behavior of TPA derivatives was investigated with temperature-dependent CD spectroscopy. Upon cooling the solution, the assembly of $\mathbf{A_{\text{-}p}}$ was showed at higher temperature than that of $\mathbf{A_{12}}$, while $\mathbf{A_{\text{-}m}}$ had the lowest elongation temperature (T_e, Figure 4c). It revealed that long linear alkyls at *meta*-position increased T_e while at *para*-position reduced. As similar analysis was valuable for chiral sergeants, T_e increased as the increment of chiral side chains at *meta*-position while the sterogenic center at *para*-position seemed to decrease the value of T_e (Figure 4d). It indicates that the stability of molecular stacks is not simply related to the number of chiral side chains present in a molecule.

Previously, it was well known that branched chiral chains led to less stable stacks than linear chain. However, the chiral sergeants $\mathbf{C_3(\mathit{S})}$ showed higher T_e than the achiral analogue $\mathbf{A_{12}}$, in spite of its nine-branched chiral alkyl. This is the first example that the branching promotes to aggregate at higher temperature compared to its achiral analogues.

These phenomena could be strongly related to the propeller conformation of central aromatics. In the monomer state, both of inner and outer benzene rings could rotate freely (Figure 4e). However, as shown in DFT calculation and VCD results, the conformation of central aromatics was enforced to adopt the chiral propeller structure in the helical supramolecular fibers (Figure 3b,c). During the formation of supramolecular nuclei, the side chains at *meta*-position was getting closer to those of vicinal stacks and intermolecularly crushed to one another. Simultaneously, the rotation of outer phenyls restrained and exhibited one of propeller conformation by ensuring the formation of hydrogen bonds. In other words, the formation of supramolecular nuclei was strongly facilitated by the intermolecular interactions of side chains at *meta*-position.

On the other hand, the aromactic propeller of achiral compounds presented the racemate of *P*- and *M*-helicity with no preferable propeller conformation in the assemblies. However, adding asymmetric elements into the side chains, the propeller structure was biased to more favorable helicity in the assembly. It revealed that the supramolecular nuclei were found to aggregate more smoothly with the presence of chiral side chains at *meta*-position of outer benzene blades. Although point chirality at the side chains expected to give insignificant effect on the far-off TPA core, it would indirectly contribute to control the chirality of a TPA propeller owing to the conjugation between the TPA core and the outer phenyls via amide linkages.

In solid state, the phase transitions and thermal behaviors of propeller-like TPA derivatives were summarized in Table 1. DSC and XRD analysis of TPA analogues showed LC mesophases and hexagonal columnar assemblies in a wide temperature range. For example, $\mathbf{A_{12}}$ displayed LC mesophase under 156 ºC through room temperature and typical XRD patterns of hexagonal columnar assembly (Figure 5b). By variable-temperature infrared spectroscopy, I successfully confirmed that hydrogen bonds supported these columnar assemblies through 3-folded amide units presented in a molecule (Figure 5a). The characteristic vibrational bands of amide bonds on the molecule shifted discontinuously to lower wavenumbers at the isotropic melt-to-LC phase transition of the molecules.

In POM measurement under crossed polarizers, LC mesophase of TPA derivatives showed a characteristic fan texture corresponded to hexagonal columnar assembly. Moreover, they exhibited the homeotropic alignment in the sandwich-typed glass cell composed of patterned ITO electrodes at electric field applied as 20 V_{pp} μm^{-1} at near T_m (Figure 5c). The alignment was sustained for a long time after removing electric field. Subsequently, heating up to isotropic melt state and cooling to LC mesophase recovered the random orientation.

A_{-m}, which was reduced long alkyl at one of *meta*-positions, showed higher melting temperature (T_m) than that of **A_{12}** while **A_{-p}** reached isotropic melt at lower temperature. It indicated that the position of long linear alkyls affected to LC assemblies, which was similar as the supramolecular assemblies in diluted solution. However, chiral TPA analogues showed similar T_m of each other. It revealed that the position and number of chiral chains was not strongly related the stability of LC assembly.

The difference of T_m depending on the structure of peripheral paraffinic wedges could be estimated by the assumption for the spatial effect of side chains on supramolecular nucleation in diluted solution (*vide supra*). However, it is noteworthy that the molecular behavior discriminates from the supramolecular equilibrium states such as elongation, nucleation and disassembly at T_e in cyclohexane. In LC mesophase below the T_m, all molecules formed columnar assemblies through hydrogen bonding of amide units and interdigitation of peripheral alkyls. It indicates that T_m reflects the stability of columnar assembly in LC mesophase. Upon heating, the side chains at the *meta*-position could be allowed to clash with one another intermolecularly for free rotation of outer phenyls. As a result, the lack of long alkyls at *meta*-position reduced intermolecular interactions and exhibited higher T_m. On the other hand, the branching in the chiral side chain triggers steric hindrances and the intermolecular interaction on columnar assembly was weakened, which resulted in lower T_m of TPA analogues with chiral side chain. However, it is noteworthy that **C_{1p}(*S*)** exhibits slightly higher T_m than the other chiral analogues due to the linear alkyls at meta-position. It indicates that the steric hindrance at meta-position is crucial for phase transition of propeller-shaped TPA derivatives in LC mesophase.

In conclusion, I have demonstrated that the LC TPAs responsive to electric field through hexagonal columnar assembly and the unprecedented amplification of supramolecular chirality of TPA derivatives originated by unique feature of propeller-shaped aromatic core. By investigating the self-assembly behavior of individual TPA compounds, side chains at *meta*-position of outer phenyls and its stereogenic centers affected the supramolecular assemblies and induced the world best chiral amplification. The systematic study of this unique system is not only promising for the growing field of molecular organization but also interesting for the control of supramolecular chirality in various applications.