

Supramolecular Polymorphism of the Hydrogen-Bonded C_3 -Symmetrical Hexadehydrotribenzo[12]annulene Derivative

Yotaro Kasahara, Takashi Takeda,* Shun Dekura, Yoshiki Ishii, Hayato Anetai, Atsuro Takai, Ichiro Hisaki, Masayuki Takeuchi, and Tomoyuki Akutagawa*

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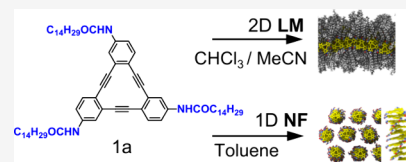


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ABSTRACT: The C_3 -symmetric hexadehydrotribenzo[12]annulene ([12]DBA) derivative (**1a**) with three tetradecylamide ($-\text{NHCOC}_{14}\text{H}_{29}$) chains capable of hydrogen-bonding interaction formed either a two-dimensional lamellar (LM) or a one-dimensional (1D) nanofiber (NF) molecular assembly, depending on the association state of the amide hydrogen bonds in the solution phase. The intermolecular amide hydrogen-bonding modes in the LM and NF structures were different from each other. The NF structure was metastable, 2.2 kJ mol $^{-1}$ less stable than that of the LM structure, and was obtained through organogel formation. In CHCl_3 , **1a** exhibited a 1D association behavior following the isodesmic model ($K = 2.18 \times 10^3 \text{ M}^{-1}$) due to intermolecular amide hydrogen bonds, whereas the presence of CH_3CN inhibited this association state. The NF structure had larger amplitude dynamics about the polar amide group than that of the LM structure, undergoing a phase transition from the NF to the LM structure upon heating. The absorption spectra of NF and solid-state LM were different from each other, exhibiting different optical properties. The coexistence of intermolecular amide hydrogen bonds and van der Waals interactions among the C_3 -symmetric molecules resulted in polymorphic phenomena, where energetically similar molecular assemblies were expressed.



INTRODUCTION

The packing structures of organic compounds in molecular assemblies are determined by various intermolecular interactions and are closely related to physical properties such as ionic conductivity,^{1–5} electrical conductivity,^{6–11} adsorption characteristics,^{12–14} optical properties,^{15,16} dielectric properties,^{17–21} and mechanical properties.^{22–24} In molecular crystals, multiple intermolecular interactions, including electrostatic interaction, hydrogen bonding, charge transfer, and van der Waals interaction, coexist to form the thermodynamically stable molecular assembly. However, when there are energetically comparable stable structures, it has been known to show polymorphism, depending on the crystallization conditions. Crystal polymorphism is critical in the fields of the manifestation of pharmacological effects, the folding/misfolding of proteins from a biological perspective,^{25–27} crystallization in food and pharmaceutical plant engineering,^{28,29} and the morphological control of inorganic nanomaterials.³⁰ From controlling physical properties in organic materials, the regulation of crystal polymorphism is also a significant research challenge. Crystal polymorphism is often observed in systems with high conformational freedom of molecules or systems where intermolecular interaction energies are similar. It has been reported in both single-component and binary molecular crystals.^{31–38} For example, in benzyl diaminodicyanopyrazine derivatives, the diversity of intermolecular hydrogen bonds and molecular conformational freedom became the origin of crystal polymorphism.³¹ Similarly, in hydrogen-bonded organic framework (HOF) crystals formed by bis-urea macrocycles or

dibromo-pyrazinoquinoxaline derivatives, molecular assembly structures vary depending on the crystallization solvent.^{33,35} The polarity and dielectric constant of the crystallization solvent influence intermolecular hydrogen-bonding interactions, modulating the energy of the stable structure and thereby causing crystal polymorphism.

In the context of nanoscale molecular assemblies, the control of nanostructures using self-assembly pathways has been reported by Meijer et al., and they demonstrated that the pathway complexity of supramolecular polymers could be controlled by external factors such as solvent polarity, concentration, temperature, additives, stirring speed, and sonication power.³⁹ Recently, numerous studies have focused on the kinetic and thermodynamic control of nanoscale molecular assemblies, such as in-living supramolecular polymerization.^{40–52} Many of these self-assembling π -conjugated molecules incorporated alkylamide or urea units and a large π -plane in their molecular structures, forming intermolecular hydrogen bonds and π - π interaction in solution. Sugiyasu et al. reported that by kinetically controlling the formation of *H*- and *J*-aggregates by strong π stacks of porphyrin derivatives,⁴⁴ they were able to selectively create

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zero-dimensional (0D) nanoparticle structures, 1D nanofiber structures, and two-dimensional (2D) sheet structures. In general, symmetric π -electron compounds and effective π -stacking interactions are at work, and furthermore, intermolecular hydrogen bonds lead to the formation of stable supramolecular structures. Studies on kinetic control of supramolecular polymorphs have been carried out.^{43,53–55} The self-assembly of π -conjugated molecules and control of the evaporation rate of solvents have been examined in order to form different nanostructures. In particular, the assembly of hydrogen-bonded supramolecular polymers depends on the control of the nucleation process by temperature and concentration, and hierarchical structure formation with a chirality transition is also realized. These studies demonstrate the importance of kinetic control by external stimuli such as temperature, solvent, light, and concentration.

Molecular symmetry is a critical factor in determining stable molecular assembly structures because it is closely related to the strength and directionality of intermolecular interactions. The π -electron frameworks that have been used so far to control molecular self-assembly processes are molecules based on the 2-fold symmetry, such as porphyrins and perylenebisimides.^{41–46,48,56,57} For example, the C_3 -symmetric trimesic acid can form hydrogen-bonded hexamers with a honeycomb structure or zigzag 1D hydrogen-bonded chains, depending on the crystallization solvent.^{58–60} Recently, by designing substituents of hydrogen-bonded C_3 -symmetric molecules, single crystals with space groups based on packing modes reflecting molecular symmetry, such as $R\bar{3}$, $P2_13$, and $R3c$, have been reported.^{61–63} Molecular systems are capable of forming molecular assemblies with 3-fold symmetry and providing a field to express unique frustrated properties. Therefore, C_3 -symmetric molecules are expected to form different molecular arrangements compared to the molecules with C_2 -axis, potentially leading to more complex hydrogen bond network. A frustrated intermolecular hydrogen bond network with 3-fold symmetry is expected to have the potential to control its molecular assembly structure and physical properties in response to external fields such as crystallization solvents and thermal energy. In addition, C_3 -symmetry is of interest as a platform for frustrated physical properties, such as spin and charge ordering.^{64–67} From the perspective of physical properties, it is crucial to explore what types of intermolecular interactions can be utilized to design molecular assembly structures while maintaining C_3 -symmetric molecules.

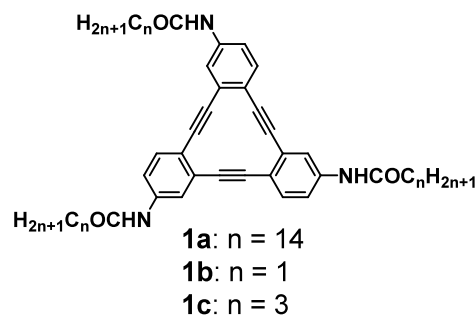
We have focused on C_3 -symmetric hexadehydrotribenzo[12]annulene ([12]DBA) and conducted studies on its molecular assembly structures. [12]DBA is a planar π -molecule that features a central cavity surrounded by three triple bonds ($-C\equiv C-$) and represents a substructure of graphyne, a theoretically proposed carbon allotrope.^{68–70} Previous studies investigated the optical properties, aromaticity, redox properties, and single-molecule conductivity of [12]DBA derivatives.^{71–73} Single-crystal X-ray structural analysis of [12]DBA revealed a herringbone packing structure driven by $C-H\cdots\pi$ interactions, without effective $\pi-\pi$ interactions.⁷⁴ In contrast, [12]DBA derivatives with substituents such as carboxyl groups introduced at 2-, 6-, 10- or 2-, 3-, 6-, 7-, 10-, 11-positions exhibited diverse crystal structures, including 1D columns,^{62,63,75} 2D layers,^{63,71,76,77} three-dimensional (3D) tetrahedral frameworks without π -stacking,⁶³ and 0D dimers.^{78,79} Additionally, molecular assembly structures such as 1D columnar liquid crystals,⁸⁰ molecular glasses,⁷⁸ and

nanostructures^{81–83} have been reported. This structural diversity arose from the intermolecular interactions and steric hindrance between substituents introduced around the C_3 -symmetric molecule, which determined the packing structures. Therefore, the design of substituents on the C_3 -symmetric [12]DBA π -core is a critical factor in controlling molecular arrangements.

Among the various substituents, extended π -electron compounds with alkylamide chains ($-NHCOC_nH_{2n+1}$) form intermolecular amide hydrogen bonds and assemble into distinctive 1D structures, such as columnar liquid-crystalline phases and organogels.^{84–86} In liquid-crystalline phases, alkylamide chains enable polarization reversal through hydrogen bond inversion under an applied electric field, resulting in ferroelectricity with hysteresis in the polarization electric field ($P-E$) curve. The multifunctional ferroelectric materials have been developed by introducing alkylamide chains into functional π -electron frameworks, such as pyrene, azobenzene, and benzothienobenzothiophene.^{87–93} While many alkylamine-substituted π -electron compounds form hydrogen-bonded 1D columnar structures, the use of nonplanar π -cores, such as helicenes, enables the formation of lamellar structures through 2D amide hydrogen-bonding interaction.⁸⁸ Controlling the intermolecular amide hydrogen bonds between alkylamide chains is effective for regulating the arrangement of π -electron cores with diverse symmetries and achieving physical properties. On the other hand, as explained earlier, effective π -stacking interactions between [12]DBA π -cores do not work due to the presence of molecular-centered pores, and it will be interesting to see the coexistence of a frustrated amide hydrogen bond site (formation of 1-, 2-, and 3-point hydrogen bonds), which acts as positive feedback for intermolecular interactions characteristic of molecules with C_3 -symmetry. The coexistence of a homogeneous π -stacking structure of the [12]DBA π -core, which is negative feedback, is of interest in what thermodynamic equilibrium states may arise. Such structure formation originating from a molecular conformation with unique C_3 -symmetry may provide important insights into the control of the structure and properties of supramolecular polymers.

In this study, we designed a derivative **1a** with C_3 -symmetry by introducing three tetradecylamide chains ($-NHCOC_{14}H_{29}$) and investigated its molecular assembly structures and physical properties (Scheme 1). As mentioned earlier, $\pi-\pi$ interactions between [12]DBA π -cores are less effective than the interactions of substituents, making it likely that diverse molecular arrangements would emerge driven by intermolecular hydrogen-bonding amide groups. Our study revealed that

Scheme 1. Chemical Structures of Alkylamide-Substituted [12]DBA Derivatives of 1a, 1b, and 1c



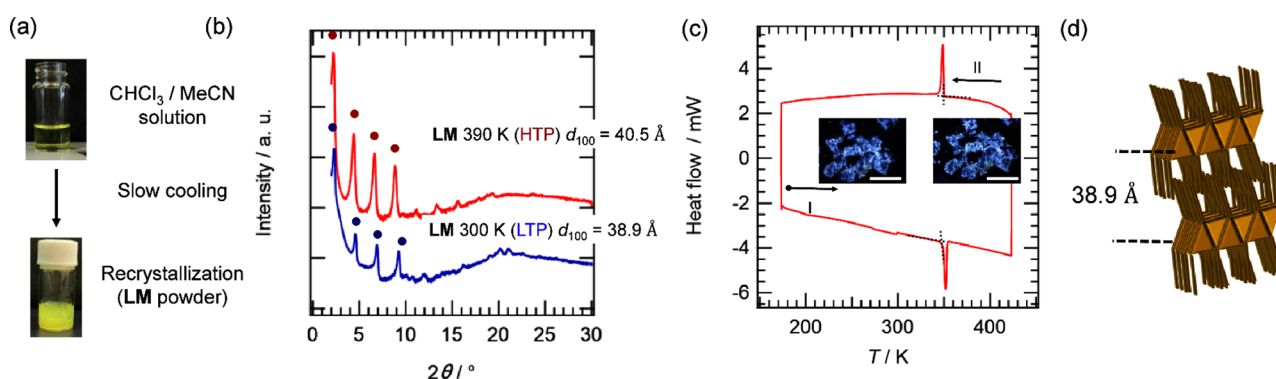


Figure 1. Phase transition behavior and molecular assembly structure of the LM structure formed by crystalline powder **1a**. (a) Crystalline powder with an LM structure obtained from a CHCl_3 – CH_3CN mixed solution. (b) Temperature-dependent PXRD patterns. Blue dots (LTP) and red dots (HTP) indicate diffraction peaks that can be attributed to the lamellar periodicity. (c) DSC curve of crystalline powder **1a** and the POM images of LTP and HTP under cross-Nicols optical arrangement (scale bar is 200 μm). (d) Schematic diagram of molecular arrangement of **1a** in the LM structure.

the aggregation state of **1a** in solution changes depending on the solvent, resulting in molecular assemblies that switch between a 2D lamellar structure (LM) and a 1D nanofiber structure (NF). We evaluated the phase transition behavior, optical properties, and dielectric properties, of these LM and NF structures formed by **1a**. Furthermore, by assessing the aggregation behavior of **1a** in the solution phase, we explored the solvent-dependent formation of these molecular assemblies.

RESULTS AND DISCUSSION

Synthesis and Electronic Structure 1a. Compound **1a** was prepared through amidation of **2**,⁷² followed by desilylation under mildly basic conditions and cyclotrimerization via a cross-coupling reaction (see Scheme S1). Recrystallization of **1a** from a chloroform (CHCl_3)–acetonitrile (CH_3CN) mixed solvent yielded a yellow crystalline powder, which was subsequently used for its structural analysis and physical properties (Figure 1a). **1a** exhibited good solubility in CHCl_3 , dichloromethane, tetrahydrofuran, and dioxane, while it dissolved in methanol (MeOH), ethanol (EtOH), 2-propanol, and dimethyl sulfoxide (DMSO) only upon heating. On the other hand, **1a** showed poor solubility in CH_3CN and hexane, and it formed organogels in heptane and toluene.

The electronic state of molecule **1a** was investigated using cyclic voltammetry (CV; Figure S2). The CV curve showed an irreversible oxidation peak at +1.38 V (vs SCE in CH_2Cl_2 , 0.1 M TBABF₄), indicating the +0.50 V anodic shift compared to tris(dialkylamino)-substituted [12]DBA.⁷¹ This shift suggests that the electron-donating ability of **1a** decreased due to the presence of electron-withdrawing carbonyl groups. The optimized molecular structure and electronic structure of the methylamide ($-\text{NHCOCH}_3$) derivative **1b** (Scheme 1) were determined using theoretical DFT calculations with the B3LYP functional and a 6-31G(d) basis set (Figure S3). The HOMO and LUMO of **1b** were -5.45 and -2.38 eV, respectively, with their orbital extending across the entire threefold symmetric [12]DBA framework. Compared to the [12]DBA derivative,⁷¹ the electron-donating ability of **1b** was lower than those of both the tris(dimethylamino)-substituted [12]DBA and the unsubstituted one, which is consistent with the CV measurements. On the other hand, the orbitals of HOMO–1 and LUMO+1 were doubly degenerate, breaking the threefold

symmetry, and their energy levels were -6.21 and -1.39 eV, respectively (Figure S3).

Molecular Assembly Structure and Phase Transition Behavior of Crystalline Powder. To evaluate the thermal stability and phase transition behavior of the crystalline powder **1a** obtained by recrystallization from a CHCl_3 – CH_3CN mixed solvent, thermogravimetry (TG), differential scanning calorimetry (DSC), polarized optical microscopy (POM) observation, and powder X-ray diffraction (PXRD) measurements were performed. The TG curve of crystalline powder **1a** showed a weight loss due to thermal decomposition around 468 K (Figure S4a). The PXRD pattern of powder **1a** exhibited multiple diffraction peaks, confirming its high crystallinity (blue line in Figure 1b and Table S1). The diffraction peak at $2\theta = 2.27^\circ$ corresponded to a periodicity of $d_{100} = 38.9$ Å, and its higher diffractions corresponding to the 200, 300, and 400 indices were observed at $2\theta = 4.59$, 6.92 , and 9.21° , respectively. Therefore, the crystalline powder **1a** was attributed to the LM structure with a periodicity of $d = 38.9$ Å. The maximum molecular length of **1a** (~ 47 Å) was about 9 Å longer than the lamellar periodicity of $d = 38.9$ Å (Figure S5), suggesting that part of the alkyl chains adopt a gauche conformation or are arranged in an interdigitated structure (Figure 1d). The IR spectra at the LM structure at 298 K show band A attributed to the C–H asymmetric stretching vibration ($\nu_{\text{C-H}}$) at 2918 cm^{-1} and band B attributed to C–H symmetric $\nu_{\text{C-H}} = 2850\text{ cm}^{-1}$ (Figure S7a). It is known that when an alkyl chain adopts a gauche conformation, its reduced mass for C–H stretching vibration decreases and its vibrational bands shift to high wavenumber.⁹⁴ In addition, band A of all-trans alkanes is known to exhibit a stretching vibrational band at 2918 cm^{-1} . Therefore, the alkyl chains in the LM structure are all-trans conformations without thermal fluctuation.

The DSC curve showed a reversible phase transition peak at around 350 K (Figure 1c). The transition enthalpy (ΔH) and transition entropy (ΔS) associated with this phase transition were 20.1 kJ mol^{-1} and $57.4\text{ J K}^{-1}\text{ mol}^{-1}$, respectively. The POM images revealed birefringence in both the low-temperature phase (LTP) and the high-temperature phase (HTP) (inset in Figure 1c), indicating that both phases were crystalline states with an orientational order. The temperature-dependent PXRD pattern of the HTP phase showed diffraction peaks consistent with the same periodicity in the

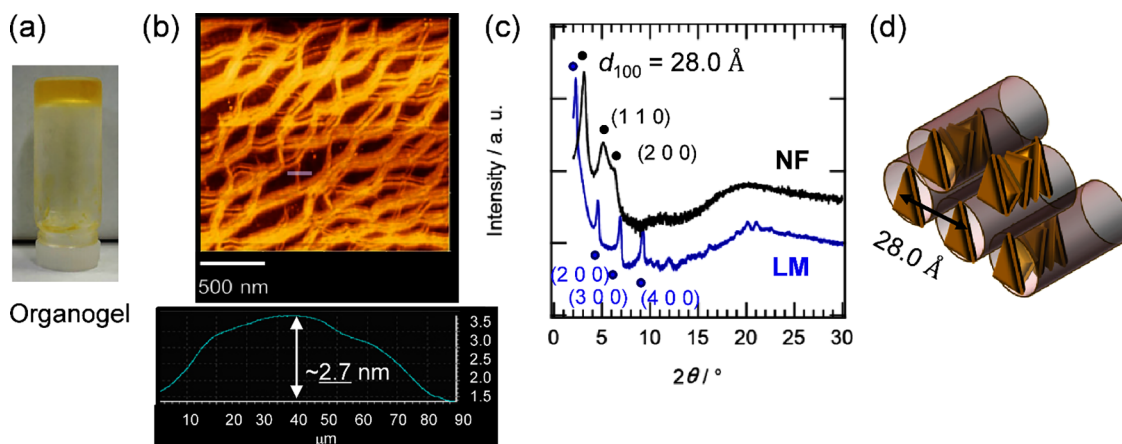


Figure 2. NF structures are formed by the OG of **1a**. (a) Photograph of the OG obtained from a heptane solution of **1a** with a concentration of 23.0 mM. (b) AFM image of the reticulated nanofibers on a SiO₂ substrate. The spin-coated film was obtained on a Si/SiO₂ substrate by using a toluene solution (100 μ M) at a rotary speed of 3000 rpm. (c) PXRD patterns of the LM and NF structures at 298 K. The LM structure was obtained as a powder sample through recrystallization from a CHCl₃–CH₃CN mixed solvent, while the NF structure was prepared as a drop-cast film on a glass substrate using a toluene solution. Blue and black dots correspond to reflection peaks attributable to the hexagonal NF and LM structures, respectively. (d) Schematic illustration of the molecular arrangement within the NF structure.

LTP phase, confirming that the LM structure was maintained (Figure 1b and Table S1). In the HTP phase, the diffraction peak at $2\theta = 2.18^\circ$, corresponding to $d_{100} = 40.5$ Å, was observed. Higher-order diffraction peaks corresponding to 200, 300, and 400 indices were found at $2\theta = 4.45, 6.65,$ and 8.87° , respectively. The d_{100} of the HTP phase was about 1.5 Å longer than that of the LTP phase, which was attributed to increased thermal fluctuations of the alkyl chains, leading to an increased correlation length of the LM structure. These results demonstrated that crystalline powder **1a** undergoes a solid-to-solid phase transition (LTP to HTP) around 350 K while maintaining the LM structure.

To understand the molecular packing and intermolecular interactions in the LM structure, the crystal structure of the propylamide derivative **1c** was evaluated (Scheme 1 and Figure S6).⁶³ In the *ac* plane, there were no significant lateral intermolecular interactions between the [12]DBA π -cores of molecule **1c**, as they were surrounded by alkyl chains (Figure S6a). Along the *a* + *b* axis of the unit cell, the [12]DBA π -cores alternated in orientation, rotating by 180°. Similarly, along the *b* + *c* axis, the [12]DBA π -cores rotated approximately 90° relative to each other, forming a zigzag arrangement with a slipped π -stack (Figure S6c). The average distance between π -planes of the [12]DBA π -cores was 3.36 Å, which is close to the sum of the van der Waals radii of the carbon atoms (3.40 Å). Along the *c*-axis of the unit cell, the molecular packing arrangement exhibited a doubled periodicity for [12]DBA, with half of the *c*-axis length (15.6878(6) Å), corresponding to the lamellar structure (Figures S6a,b). Of the three amide groups in **1c**, the two sites formed the 2D N–H...O= hydrogen bonds with $d_{N\cdots O}$ distances of 2.822(2) and 3.009(2) Å (Figure S6d), while the remaining one amide group did not participate in intermolecular hydrogen bonding with the closest $d_{N\cdots O} = 4.676(4)$ Å. In the crystal, molecule **1c** formed the π -stacked LM structure with significantly slipped [12]DBA π -cores, stabilized by two sites of intermolecular amide hydrogen bonds and π -stacking interactions.

The LM structure observed for the powdered sample of **1a** is also considered to form a lamellar arrangement similar to that of **1c**. In the LM structure of **1a**, unlike **1c**, the d_{100} periodicity corresponds to the length of a molecule. This is because the

alkyl chains in **1a** are sufficiently long that there is no need for packing with the molecular planes tilted 90° to each other as seen in **1c** (Figure S6b). The IR spectrum of the LM structure at 298 K showed N–H stretching vibration bands (ν_{NH}) at 3320, 3290, and 3250 cm^{−1} (Figure S7b), corresponding to the formation of intermolecular amide hydrogen bonds. Additionally, the isolated amide group not involved in intermolecular hydrogen-bonding interactions exhibited an ν_{NH} band on the higher wavenumber at 3410 cm^{−1}. The C=O stretching vibrational band (ν_{CO}) corresponding to the formation of intermolecular amide hydrogen bonds was observed at 1668 cm^{−1}, while the ν_{CO} band for an isolated amide group not involved in intermolecular amide hydrogen bonds was identified at 1693 cm^{−1} on the high wavenumber. The hydrogen bond accepting carbonyl group showed a similar trend to the energy shift of the hydrogen-bonding donor of the N–H group (Figure S7b). This spectrum was consistent with the hydrogen-bonding patterns observed in the single-crystal X-ray structural analysis of **1c**. While **1a** has longer alkyl chains compared to **1c**, it similarly forms 1D π -stacked columns with significant slipped π -planes of [12]DBA, which are arranged into a 2D LM structure.

Formation of Organogel and Its Molecular Assembly.

The crystalline powder **1a** obtained from a CHCl₃–CH₃CN mixed solvent formed the LM structure via an intermolecular amide hydrogen-bonding interaction. In contrast, when **1a** was dissolved in nonpolar organic solvents such as heptane or toluene under heating and then cooled, it formed an organogel (OG), suggesting the formation of 1D molecular assembly nanostructures (Figure 2a). To observe the molecular assembly nanostructures within the OG, a spin-coated film of **1a** was prepared on a Si/SiO₂ substrate using a toluene solution, followed by AFM observation. As a result, NF with a height of 2.7 nm was observed (Figure 2b). Therefore, **1a** forms NF structures in nonpolar solvents, which differ from the LM structure exhibited by the crystalline powder obtained from the CHCl₃–CH₃CN mixed solvent. The C₃-symmetric molecule **1a** was capable of forming both NF and LM structures depending on the conditions for the molecular assemblies.

To investigate the molecular arrangement within the NF structure formed by **1a**, PXRD patterns were measured for a drop-cast film prepared from a toluene solution. The results revealed a diffraction pattern attributable to a hexagonal arrangement with a d_{100} spacing of approximately 28.0 Å (Figure 2c and Table S2), which was shorter than d_{100} LM. Amide-type hydrogen-bonding [12]DBA derivatives have been reported to form discrete closed-hydrogen-bonded dimer structures, with π -stacking distances of 3.25–3.52 Å.⁷⁹ On the other hand, the formation of organogel suggests the presence of long-range 1D hydrogen-bonding interactions rather than a discrete dimer structure, consistent with the formation of 1D column structures by amide hydrogen bonding. 1D columns are hexagonally aligned, and a broad reflection peak is observed at $2\theta \sim 20^\circ$, indicating the thermally fluctuated disordered columnar structure.

A drop-cast film of the NF structure was prepared on a KBr substrate, and IR spectroscopy was employed to evaluate the intermolecular amide hydrogen-bonding interactions and the fluctuation of the alkyl chains. The ν_{NH} bands were observed at 3250 and 3220 cm^{-1} , and the ν_{CO} band at 1650 cm^{-1} , indicating that both are involved in intermolecular amide hydrogen bonding, while the isolated ν_{NH} band, which is not involved in the intermolecular amide hydrogen bonding observed in the LM structure, was not detected. The ν_{NH} and ν_{CO} bands of the NF structure exhibited lower wavenumbers compared to those of the LM structure (Figure S7b,c), indicating that the intermolecular amide hydrogen bonds in the NF structure were stronger than those in the LM structure. These results suggest that the NF structure of **1a** formed the 1D molecular assemblies facilitated by the formation of stronger intermolecular amide hydrogen bonds compared to the LM structure, resulting in a hexagonal arrangement. In the NF structure, band A and band B of ν_{CH} are observed at 2852 and 2922 cm^{-1} , respectively. It is known that when an alkyl chain takes a gauche conformation, its vibrational bands are shifted to higher wavenumbers due to a lower reduced mass for C–H stretching vibrations.⁹⁴ Therefore, the observed ν_{CH} energy in the NF structure is shifted to higher wavenumbers than in the LM structure, consistent with the gauche conformation being consistent with a disordered structure that is coexisting.

To understand the molecular arrangement and intermolecular interactions within the NF structure, quantum chemical calculations were performed on a pentamer model of the methylamide derivative **1b** using DFT calculations with the M05 functional and the 6-31G (d,p) basis set (Scheme 1 and Figure S8). The optimized structure was the 1D molecular assembly with a helical arrangement, where the three methylamide groups formed intermolecular amide hydrogen bonds. The intermolecular amide hydrogen bond distances were observed at $d_{\text{N–O}} = 2.86\text{--}2.87$ Å, and all amide groups contributed equally to the formation of intermolecular hydrogen bonds. This finding was consistent with the IR spectrum of the NF structure of **1a**, which indicated that all amide groups were involved in intermolecular hydrogen bonding (Figure S7). In the single-crystal structures of [12]DBA derivatives with amide units,^{62,79} the helical hydrogen bond networks like that optimized structure were observed. Thus, it was demonstrated that the mode of the intermolecular amide hydrogen-bonding interaction in **1a** changes depending on the crystallization solvent, allowing the formation of both NF and LM structures.

NF–LM Phase Transition. The thermal stability and phase transition behavior of the NF structure formed by **1a** were evaluated using TG, DSC, and variable-temperature PXRD. The TG curve of the NF structure showed no weight loss up to 485 K, indicating the absence of a crystallization solvent (Figure S4b). The DSC chart of the NF structure exhibited a small reversible phase transition peak at 320 K during the scan up to 423 K. During heating up to 463 K (thermal cycle III in Figure 3a), the DSC chart showed the

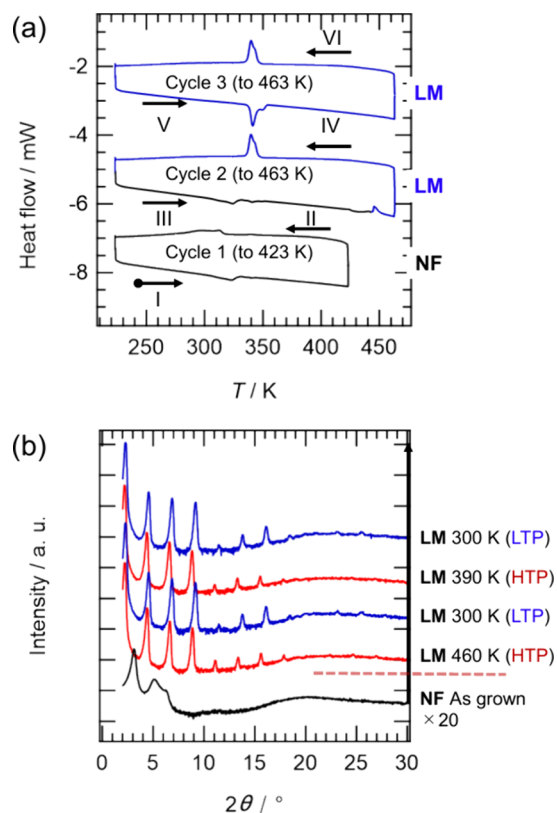


Figure 3. Phase transition behavior of the NF structure formed by **1a**. (a) DSC curve of the NF structure. (b) Variable-temperature PXRD pattern of the NF structure.

peak at 320 K and an irreversible exothermic peak around 440 K with $\Delta H = -2.2$ kJ mol^{-1} . During the cooling process from 463 K (thermal cycle IV in Figure 3a), a new exothermic peak appeared around 350 K with $\Delta H = -17$ kJ mol^{-1} . In subsequent thermal cycles V and VI in Figure 3a, a reversible phase transition peak with $\Delta H = \pm 17$ kJ mol^{-1} was observed around 350 K, consistent with the DSC chart of the LM structure. The variable-temperature PXRD patterns of the NF structure revealed that heating to 460 K caused a transition from the hexagonal structure observed at 298 K to the diffraction pattern corresponding to the HTP phase of the LM structure (Figure 3b). Additionally, repeated cooling–heating thermal cycles showed changes in correlation length corresponding to the HTP–LTP phase transition of the LM structure. These results demonstrate that the metastable NF structure undergoes an irreversible phase transition to the energetically more stable LM structure (2.2 kJ mol^{-1}) around 440 K. In van der Waals crystals formed by phenylanthracene derivatives, a phase transition from a metastable single crystal to a thermodynamically stable single crystal has been reported, accompanied by an exothermic behavior of 19.7 kJ mol^{-1} .³⁸ In

addition, an irreversible phase transition from a metastable 1D channel structure to a stable packing structure with no void space has also been reported for hydrogen-bonded macrocycle derivatives with exothermic behavior of several kJ mol^{-1} .³⁵ In the phase transition from NF to LM structures, the number of amide hydrogen bonds of **1a** as a stabilizing factor is reduced to form a packing structure favorable to the LM structure. The metastable NF structure is considered to be formed by kinetic trapping by three-point amide hydrogen bonds in a solvent in which OG formation is possible.

Dielectric Constants of LM and NF Structures. To evaluate the dynamics in the molecular assemblies of NF and LM structures, the temperature and frequency dependence of the dielectric constant was measured using the AC impedance method (Figure 4 and Figure S9). A drop-cast film was prepared on an indium–tin oxide (ITO) electrode by using a toluene solution of **1a**, and a sandwich-type electrode cell was constructed (Figure 4a).

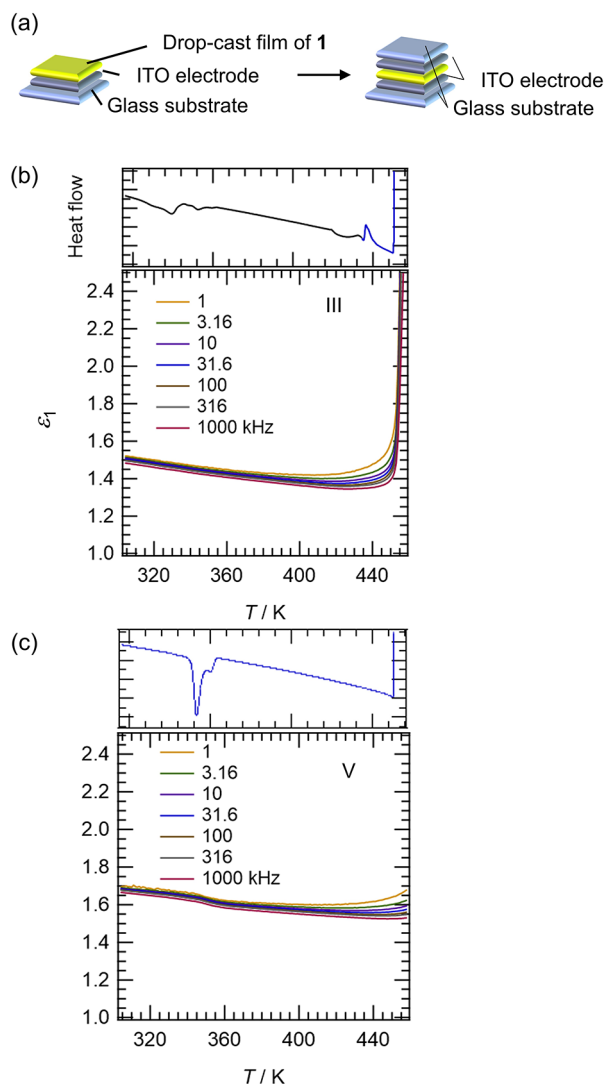


Figure 4. Frequency- and temperature-dependent real part of dielectric constants (ϵ_1) of the NF and LM structures in **1a**. (a) Schematic of the sandwich measurement cell with a thickness of 10 μm and area of 16 mm^2 . The ϵ_1 values of (b) NF structure and (c) LM structure.

For the NF structure, the real part of the dielectric constant (ϵ_1) at 300 K was 1.5, showing a slight decrease with minimal frequency dependence up to 400 K (Figures S9a,d). However, dielectric responses were observed in the low-frequency region starting around 400 K, and a significant increase in ϵ_1 was observed near the NF–LM phase transition point at approximately 440 K (Figure 4b and Figure S9c,e). The clear ϵ_1 response in the low-frequency region is attributed to the slow thermally activated motion of dipole moments within the molecular assembly, likely associated with the dynamics of the polar alkyl amide groups. For the LM structure, $\epsilon_1 = 1.7$ at 300 K was similar to the value for the NF structure at the same temperature (Figure 4c and Figure S9c,f). A slight dielectric anomaly was observed near the solid–solid phase transition temperature at approximately 350 K, with a slight decrease in the dielectric constant that was weakly frequency-dependent. However, no significant temperature- and frequency-dependent behavior was observed. These results suggest that the thermal motion of the alkyl amide groups in the LM structure was lower compared to that in the NF structure.

The dynamics of the polar amide groups observed in the dielectric constant were also confirmed by temperature-dependent IR spectra (Figure S10). Upon heating the NF structure from 313 to 448 K, the ν_{NH} bands at 3220 and 3250 cm^{-1} were broadened (Figures S7 and S10a), which corresponded well with the frequency-dependent ϵ_1 behavior (Figure 4a). At 458 K, the peak at 3220 cm^{-1} disappeared, and new ν_{NH} bands corresponding to the LM structure were observed at 3290, 3320, and 3410 cm^{-1} . This change indicates the dissociation of intermolecular amide hydrogen bonds in the NF structure and the formation of the LM structure during the NF–LM phase transition induced by heating. The dynamics of the amide groups are reduced in the LM structure compared to the NF structure. We have previously evaluated molecular dynamics in crystalline, liquid crystalline, plastic crystalline, glass phases, and their phase transitions through dielectric constants of various alkyl amide, sulfonamide, and ester-substituted molecules.^{78,86–92,95,96} In this study, we were able to correlate the polymorphism of molecular assembly structures and the dynamics of amide groups by using the temperature dependence of the dielectric constant and IR spectra.

MD Simulation for LM and NF Structures. In order to clarify structural information for the NF and LM phases of supramolecular self-assembly, we further carried out molecular dynamics (MD) simulation with all-atom resolution. Although there are difficulties for computational observations of the transform of liquid crystalline phases and the determination of transition temperature,^{97–99} the stability of self-assembly structures can be considered from observed structures in MD simulations starting with candidate structures (Figure S1).^{100,101} First, the structural candidates of NF and LM phases were found to form the self-assembly structures through our MD simulations.

The NF structures of **1a** preserved the 1D stacking configuration with the [12]DBA π -core via the π – π and hydrogen-bonding interactions (Figure 5a,c), and hydrophobic moieties covered the columnar assembly structure (Figure S1a). The distances across self-assembled [12]DBA columns were 23 $\sim$ 24 $\text{\AA}$, which underestimated the experimental values of d_{100} ($\sim$ 28.0 $\text{\AA}$) from the PXRD pattern. This difference would be due to the complete alignment of the [12]DBA columns prepared for the initial configuration of the MD

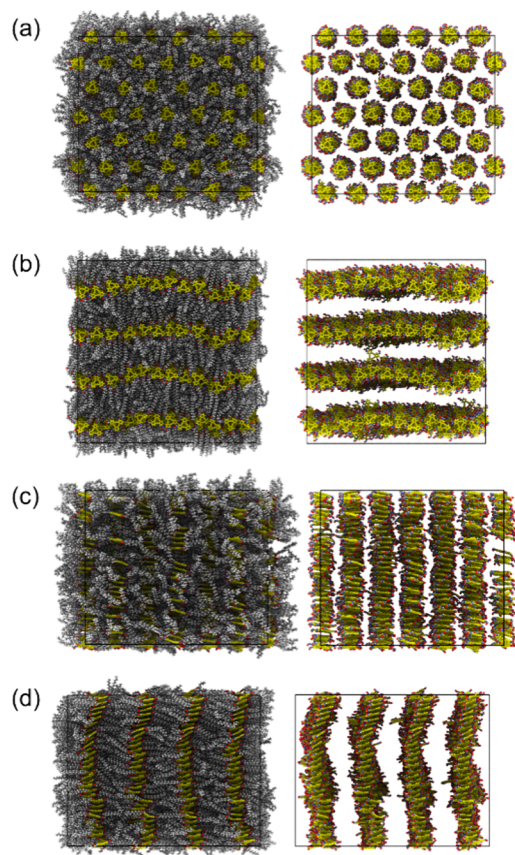


Figure 5. Simulated molecular assembly structures using MD calculations. (a–d) 3D snapshots of the self-assembly structures of NF (a, c) and LM (b, d) observed by our MD simulations. The panels of (a, b) represent the x - y plane, and those of (c, d) represent the y - z plane. The hydrophobic groups of **1a** are displayed in the left panels of (a–d), and they are now shown in their right panels. (Legend) Yellow: atoms of [12]DBA core; red: oxygen atoms; blue: nitrogen atoms; gray: carbon atoms; white: hydrogen atoms.

simulation. Thereby, this result suggests that the experimental observation of the NF structure via the drop-cast method on

the substrate surface can be considered to form a partially disordered state than the simulated NF structure. The LM structures of **1a** also kept the periodic 2D self-assembly structures (Figure 5b), and the layer of [12]DBA π -cores showed a wavy surface with the tilted [12]DBA π -cores (Figure 5b,d). The antiparallel π -stacking alignment of **1a** was well preserved through the MD simulation, and the interlayer distance of LM structures yielded 37 ~ 38 Å (Figure 51b). This value well followed the experimental d_{100} = 38.9 Å observed as the LM structure in the PXRD pattern. Since the corresponding PXRD measurement does not suggest any other structural characteristics, our MD simulation enabled us to reproduce the self-assembled LM structures investigated by PXRD.

We further focus on the intermolecular interaction of **1a** in the NF and LM structures, as observed by our MD simulations. The radial distribution functions (RDFs) among the [12]DBA π -cores of **1a** and the tilt-angle distribution between the neighboring [12]DBA π -cores were analyzed to quantify the difference in their binding interactions between NF and LM structures (Figure S11). The neighboring [12]DBA π -cores were strongly bounded in the NF structure, which resulted in the large intensity of RDF. On the contrary, the [12]DBA π -cores in the LM structure show a relatively weak intermolecular interaction. The equilibrated distances of the NF and LM structures between [12]DBA π -cores were 3.5 and 4.0 Å, respectively (Figure S11a). These specific behaviors can be interpreted as the results of whether the π - π interaction of the [12]DBA π -core and the hydrogen bonds of the amide groups work in the same direction or not. Furthermore, from the detailed analyses of hydrogen-bonding groups, the number of hydrogen bonds per **1a** was 3.16 for the NF structure and 2.17 for the LM structure. Nevertheless, the computed density for the NF structures yielded 0.9918 g cm⁻³, which was less than 0.9962 g cm⁻³ for the LM structure. These MD simulations suggest that the loss of hydrogen bonds in the LM structures slightly weakens the binding interaction among [12]DBA π -cores in comparison with the NF structure. However, the LM structure enhances the packing density with the interaction of hydrophobic moieties like molecular fastener effects (Figure 5d), and the [12]DBA π -cores of the LM

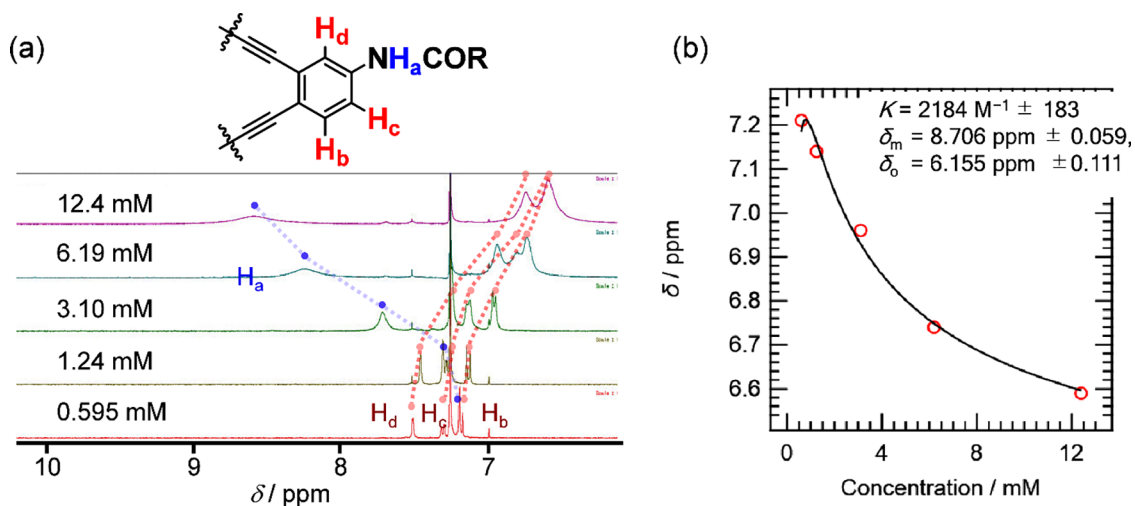


Figure 6. Aggregation behavior and solvent dependence of **1a** in the solution phase. (a) Concentration-dependent ¹H NMR spectra in CDCl₃ at 298 K. (b) Concentration vs δ_{Hb} plot of **1a** and fitting results using the isodesmic model using the fitting parameters of association constant K , the estimated value of chemical shift for the monomer δ_m , and the estimated value of chemical shift for the oligomer δ_o .

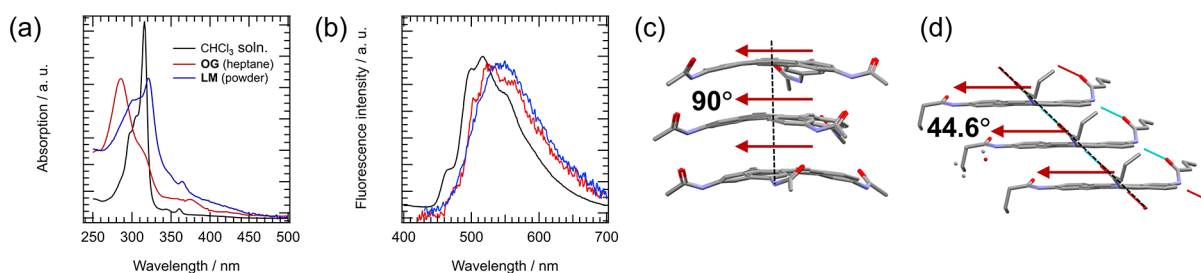


Figure 7. Absorption and emission spectra of **1a** in CHCl_3 solution with a concentration of 8.04×10^{-6} M, heptane **OG**, and crystalline powder with **LM** structure. (a) Absorption spectrum. (b) Emission spectrum. The excitation wavelength of the emission spectrum was 360 nm. (c, d) Schematic arrangement pattern of optical transition dipole moments in molecular assembly structures in (c) **OG** and (d) single-crystal **1c**.

structure were more tilted than those of **NF** structures (Figure S11b). Thereby, we can consider that competitive behaviors for the advantages of the hydrogen-bonding interaction and packing density in the **NF** and **LM** structures, respectively, provide the structural selectivity of supramolecular self-assembly structures depending on the synthesis route.

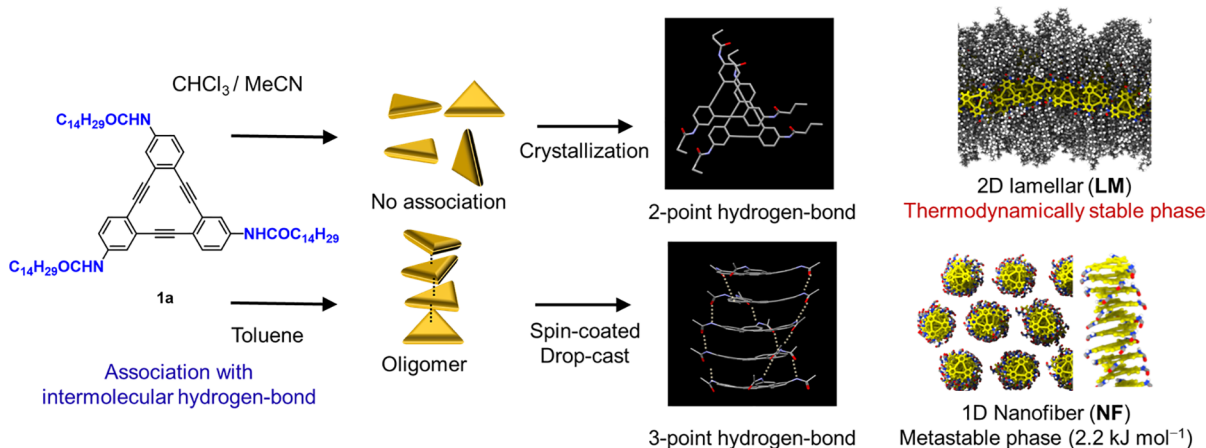
Association of 1a in Solution. To investigate the solvent effect on the aggregation state of **1a** in solution, the concentration dependence of the ^1H NMR spectra was measured in CDCl_3 and a $\text{CDCl}_3/\text{CD}_3\text{CN} = 9/1$ (v/v) mixed solvent (Figure 6 and Figure S13). In the ^1H NMR spectra in CDCl_3 , an increase in concentration led to an enhanced shielding effect on aromatic protons $\text{H}_b\text{--H}_d$, accompanied by signal broadening (Figure 6a). This result suggests the presence of the aggregation state caused by an association equilibrium with the monomer state. Fitting the concentration dependence of the δ_{Hb} values in the ^1H NMR spectra at 298 K to an isodesmic model (eq S1) showed good agreement, and the association constant was determined to be $K = 2.18 \times 10^3 \text{ M}^{-1}$ (Figure 6b).

The signal of the amide proton H_a showed changes reflecting a deshielding effect due to an intermolecular amide hydrogen-bonding interaction. Additionally, the IR spectrum of **1a** in CHCl_3 with a concentration of 4.25 mM showed an amide hydrogen-bonded ν_{NH} band at 3320 cm^{-1} and a ν_{NH} band at 3430 cm^{-1} corresponding to amide groups not involved in the hydrogen-bonding interaction (Figure S12). The concentration dependence of the ^1H NMR spectra indicated that the aggregation behavior did not reach saturation at the measured concentration. The observation of a ν_{NH} band for non-hydrogen-bonded amides suggests that molecular aggregation via intermolecular amide hydrogen-bonding interaction does not proceed to completion, which is consistent with the changes observed in the H_a signal in the ^1H NMR spectra. The IR spectrum of **1a** in toluene solution with a concentration of 4.56 mM showed ν_{NH} bands at 3260 and 3220 cm^{-1} (Figure S12), attributed to a stronger intermolecular amide hydrogen-bonding interaction compared to CHCl_3 . These findings confirmed the formation of aggregated **1a** structures through an intermolecular amide hydrogen-bonding interaction. The behavior of the amide hydrogen-bonding interaction dependent on solvent polarity is similar to the polymorphic phenomena observed in porphyrin derivatives that form supramolecular assemblies.^{44,45} This suggests that the intermolecular amide hydrogen-bonding interaction in solution is a key factor governing the solvent dependence of molecular assembly structures. On the other hand, the ^1H NMR spectra of **1a** in a more polar $\text{CDCl}_3/\text{CD}_3\text{CN} = 9/1$ (v/v) solvent mixture exhibited a behavior distinct from that in

CDCl_3 (Figure S13). Compared with the results in CDCl_3 , the peak shift and signal broadening caused by concentration changes were significantly reduced in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (Figure S14). The added CD_3CN forms intermolecular $\text{C}\equiv\text{N}\cdots\text{H}\cdots\text{N}$ hydrogen bonds between the alkyl amide groups and CD_3CN , thereby inhibiting the aggregation of **1a** through an intermolecular amide hydrogen-bonding interaction.

Optical Properties of 1a. To investigate the correlation between molecular assembly structures and optical properties, we measured the absorption and fluorescence spectra and quantum yields of **1a** in CHCl_3 solution, the **OG** state, and the crystalline powder on the KBr pellet (Figure 7a,b, Figure S15, and Table S3). In dilute CHCl_3 solution, **1a** showed an absorption maximum of around 315 nm and absorption peaks at 340 and 360 nm. This behavior was similar to that of pristine **[12]DBA** and its derivatives.⁶⁶ The absorption peaks of **1a** were assigned based on TD-DFT calculations using the B3LYP functional and the 6-31G(d,p) basis set for **1b** (Figure S16 and Table S4). The calculated $\text{S}_0 \rightarrow \text{S}_1$ optical transition (HOMO $\rightarrow$ LUMO transition) was observed at 508 nm, which was a forbidden optical transition with zero oscillator strength due to orbital symmetry. Additionally, the absorption bands at 372 nm ($\text{S}_0 \rightarrow \text{S}_{2,3}$ optical transitions) and 326 nm ($\text{S}_0 \rightarrow \text{S}_{4,5}$ optical transitions) can be attributed to the HOMO-1 $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+1 transitions, respectively. The oscillator strengths for the $\text{S}_0 \rightarrow \text{S}_{2,3}$ transitions and the $\text{S}_0 \rightarrow \text{S}_{4,5}$ transitions were 0.065 and 1.16, corresponding to the 360 and 310 nm absorption bands observed for **1a**. Molecule **1a** exhibited green emission in CHCl_3 with an emission maximum of ~ 515 nm upon excitation at 360 nm. The Stokes shift and quantum yield were $\sim 12,300 \text{ cm}^{-1}$ and 5.4%, respectively (Figure S15a,b). The emission behavior of **1a** was similar to that of previously reported **[12]DBA** derivatives.⁷³

However, absorption spectra of **1a** in each state showed differences due to the assembly state changes (Figure 7a). The absorption spectrum of **1a** in the **OG** state showed a weak peak at 370 nm. For **[12]DBA** derivatives with methoxycarbonyl-phenyl groups, it has been reported that strong interorbital interactions cause changes in the symmetry of frontier orbitals, resulting in a transition of the HOMO-LUMO oscillator strength from zero to a finite value.¹⁰² On the other hand, the absence of significant spectral changes around 365 nm in the **OG** state of **1a** suggests negligible intermolecular interactions between π -cores. However, the absorption maximum of **1a** was observed at 295 nm in the **OG** state, exhibiting a 25 nm blue shift compared to that of the solution state. The absorption spectrum of the **LM** structure in the powdered sample showed an absorption maximum at ~ 320 nm and a shoulder at ~ 360

Scheme 2. Solvent-Dependent Polymorphism Exhibited by C_3 -Symmetrical **1a**

nm, exhibiting a ~ 5 nm red shift compared to the solution state spectrum.

In order to elucidate the relationship between the chromism and the electronic structure in accordance with the structure of the molecule assemblies, we calculated the molecular orbital involved in optical transition (LUMO+5 – LUMO, HOMO – HOMO–5) for the **1b** dimer in the optimized pentamer (Figure S17) and the **1c** dimer in the single-crystal structure (Figure S18) using the M05/6-31G(d,p) basis set. In all structures, the coefficients of the frontier orbitals were localized to the monomer while maintaining the LUMO+1, LUMO, HOMO, and HOMO–1 shapes. Thus, we can conclude that the chromism is not due to a change in electronic structure depending on the molecular assembly structure. In the NF structure, the angle of the optical transition moment to the π -stacking axis is 90° , which is consistent with the formation of *H*-aggregates (Figure 7c). Therefore, this blue shift in the OG state was attributed to the formation of *H*-aggregates with the 1D arrangement of the optical transition dipole moment. These results were consistent with formation of the 1D structure stabilized by the intermolecular amide hydrogen bonding (Figure S8) in the OG state. On the other hand, in the single-crystal structure of **1c**, the angle formed by the optical transition moment with respect to the π -stacking axis is 44.6° , which is smaller than the magic angle of 54.9° . Therefore, the absorption spectrum of the LM structure is considered to be derived from the *J*-aggregate (Figure 7d). In the aggregation state, the emission maxima and quantum yields were approximately 520 nm and $\sim 5\%$, respectively, with no significant differences (Figure 7b). This is because there was almost no change in the electronic state due to π -interactions such as excimer formation.

Mechanism of Polymorphism. Scheme 2 summarizes the polymorphism of the molecular assemblies of **1a**. In toluene, the molecules **1a** are associated through intermolecular three-point amide hydrogen-bonding interaction, leading to the formation of the 1D nanofibers, and subsequently OG. The concentration of the OG, metastable NF phase was formed by the kinetics trap of the hydrogen bonds like the solvated crystals.³⁵ Upon heating, thermal activation of the dynamics of the alkylamide hydrogen bonds induced the irreversible phase transition to the LM structure, which was 2.2 kJ mol^{-1} thermodynamically more stable than NF. In contrast, in polar solvents, the formation of a three-point intermolecular amide hydrogen-bonding interaction between **1a** is inhibited,

resulting in the direct formation of the thermodynamically stable LM structure. X-ray crystallographic analysis also confirmed that the LM structure is formed when two of the three amide hydrogen-bonding sites in the molecule contribute to the formation of molecular assembly.⁶³ The intermolecular amide hydrogen bonds formed by **1a** were weaker compared to those reported for other π -electron compounds with alkyl amide substitutions.^{86,87} Slight changes in crystallization conditions modulated these intermolecular amide hydrogen bonds, resulting in the emergence of polymorphism (Figure S12).

In the molecular assemblies of [12]DBA derivatives, the interactions of the substituent have been more dominant than π – π interactions of the [12]DBA core.^{62,63,71,75–79} In 1,3,5-triazine derivatives, which are similar hydrogen-bonded threefold symmetric molecules, the effective π -stacking interaction works,⁶¹ whereas in [12]DBA derivatives, the π -stacking interaction does not work effectively due to the limited π surface area (pore) at the DBA π -core. By introduction of alkylamide groups at the molecular terminals, intermolecular amide hydrogen-bonding and van der Waals interactions were introduced as stabilizing factors in molecular assemblies, compensating for the lack of effective π – π interactions between [12]DBA π -cores. These two different types of intermolecular interactions competed, enabling the formation of molecular assemblies with similar energy states that responded to subtle external factors. Similar to C_3 -symmetrical trimesic acid, the polymorphism of molecular assemblies was determined by how the three hydrogen-bonding sites were involved in intermolecular hydrogen bonding.^{58–60} In the previous supramolecular polymers based on π -conjugated molecules with side chains such as porphyrin and PDI derivatives,^{44,48} various thermodynamically stable or metastable aggregates such as 0D nanoparticles, 1D nanofiber, and 2D nanosheets can be formed by the energy competitions between *H*- or *J*-aggregates of strong π -stack. The polymorphism based on the [12]DBA skeleton with weak π – π interactions is considered predominantly governed by the pattern of intermolecular amide hydrogen-bonding interaction. The competition between the weak π -interaction and the intermolecular amide hydrogen-bonding interaction, which can change the number of its interaction points, changed the resulting molecular assembly structure and gave rise to crystal polymorphism. This is a phenomenon characteristic of the

hydrogen bonding nature of threefold symmetric molecules [12]DBA derivative.

CONCLUSIONS

We prepared the [12]DBA derivative **1a** with a C_3 -symmetric π -electron core and hydrogen-bonding $\text{—NHCOC}_{14}\text{H}_{29}$ chains, successfully achieving selective formation of the thermodynamically metastable NF structure and the stable LM structure through control of the intermolecular amide hydrogen-bonding interaction in the solution phase. In the NF structure, three robust intermolecular amide hydrogen bonds per molecule formed, resulting in a molecular assembly structure, where 1D columns were hexagonally arranged. In contrast, the LM structure involved two intermolecular amide hydrogen bonds per molecule, contributing to the molecular assembly formation. Temperature- and frequency-dependent dielectric constants and variable-temperature IR spectra revealed differing alkylamide dynamics in the NF and LM structures. The NF structure, with larger thermally activated dynamics, exhibited the phase transition to the thermodynamically stable LM structure upon heating. The energies of LM and NF structures had a slight difference of 2.2 kJ mol^{-1} , resulting from the competition between intermolecular amide hydrogen bonding and van der Waals interactions in the closest-packing structures. The absorption spectra of the NF structure in its OG state and the LM structure differed, displaying chromism phenomena based on differences in the molecular assembly structures. The competition between intermolecular amide hydrogen bonding and van der Waals interactions in the C_3 -symmetric [12]DBA molecule-induced polymorphism. This study demonstrated the potential to develop highly sensitive sensor materials with tunable dielectric, emission, and carrier transport properties in response to subtle external stimuli. A C_3 -symmetric molecule offers an intriguing research avenue for functional material development and enables a shape-driven approach to controlling polymorphism in molecular assemblies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.5c02529>.

Experimental sections, TG charts, crystal structures, IR spectra, T - and f -dependent ϵ_2 , theoretical calculation, PXRD, and optical properties of **1a** (PDF)

AUTHOR INFORMATION

Corresponding Authors

Takashi Takeda — Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan; Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai 980-8577, Japan; Faculty of Science, Shinshu University, Matsumoto 390-8621, Japan; orcid.org/0000-0002-5254-2819; Email: takashi@shinshu-u.ac.jp

Tomoyuki Akutagawa — Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai 980-8577, Japan; Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan; orcid.org/0000-0003-3040-1078; Email: akutagawa@tohoku.ac.jp

Authors

Yotaro Kasahara — Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

Shun Dekura — Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan; Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai 980-8577, Japan; orcid.org/0000-0003-2498-6428

Yoshiki Ishii — School of Frontier Engineering, Kitasato University, Sagami-hara, Kanagawa 252-0373, Japan; orcid.org/0000-0003-0102-9326

Hayato Anetai — National Institute for Materials Science (NIMS), Tsukuba 305-0047, Japan

Atsuro Takai — National Institute for Materials Science (NIMS), Tsukuba 305-0047, Japan; orcid.org/0000-0003-3457-3352

Ichiro Hisaki — Graduate School of Engineering Science, The University of Osaka, Toyonaka, Osaka 560-8531, Japan; orcid.org/0000-0002-8170-5605

Masayuki Takeuchi — National Institute for Materials Science (NIMS), Tsukuba 305-0047, Japan; Research Center for Autonomous Systems Materialogy (ASMat), Institute of Integrated Research (IIR), Institute of Science Tokyo, Yokohama 226-8501, Japan; orcid.org/0000-0002-0207-0665

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/jacs.5c02529>

Notes

The authors declare no competing financial interest.

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