

Ring-Size Effect on Molecular Assembly Structures and Optical Properties of C_3 -Symmetrical Dehydrobenzoannulene Derivatives

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RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

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Abstract: We reported that **C8[12]DBA**, a C_3 -symmetric hexadecahydrotribenzo[12]annulene (**[12]DBA**) with a pore surrounded by three $-C\equiv C-$ bonds, forms a stable molecular glass during cooling from the liquid state when an octylbenzoate group was introduced at the molecular terminal. In this study, to understand the influence of the molecular structure of C_3 -symmetric **DBA** derivatives on molecular assembly structures and optical properties, we newly synthesized **C8[18]DBA**, which has a pore surrounded by more elongated $-C\equiv C-C\equiv C-$ bonds. Furthermore, a comparison was made with an octylbenzoate-substituted triphenylene derivative (**C8Trip**) that has C_3 symmetry and no pore at the molecular center. The strength of intermolecular interactions decreased in the order **C8[18]DBA** > **C8Trip** > **C8[12]DBA**. **C8[18]DBA** formed π -dimers and gave crystalline molecular assemblies, whereas in **C8[12]DBA**, the suppression of π - π interactions stabilized the glass state. **C8[18]DBA** did not exhibit dielectric anomalies, whereas **C8Trip** and **C8[12]DBA** showed dielectric relaxation associated with the thermal motion of the octyl ester chains. Furthermore, while **C8[12]DBA** exhibited similar fluorescence spectra in solution and solid states, both **C8[18]DBA** and **C8Trip** exhibited aggregation-induced quenching with a significant decrease in fluorescence intensity in the solid state.

1. Introduction

Between single crystals and liquids, there exist mesophases such as liquid crystal phase¹ and/or plastic crystals.^{2,3} These mesophases are in a thermally excited dynamic state where molecular rotation and diffusion are active. Recently, by precisely controlling the degrees of freedom of molecular rotation dynamics, it has become possible to show physical properties such as ferroelectricity, ion conductivity, and barocaloric effect.^{4–11} On the other hand, organic glasses without order in molecular center-of-mass position and molecular orientation suppress grain boundaries and crack formation in thin films, exhibiting high dielectric strength and excellent durability. As such, they are important materials for forming stable thin film structures in organic electronics.^{12–20} From a molecular design perspective, controlling intermolecular interactions and understanding glass formation are critical challenges.

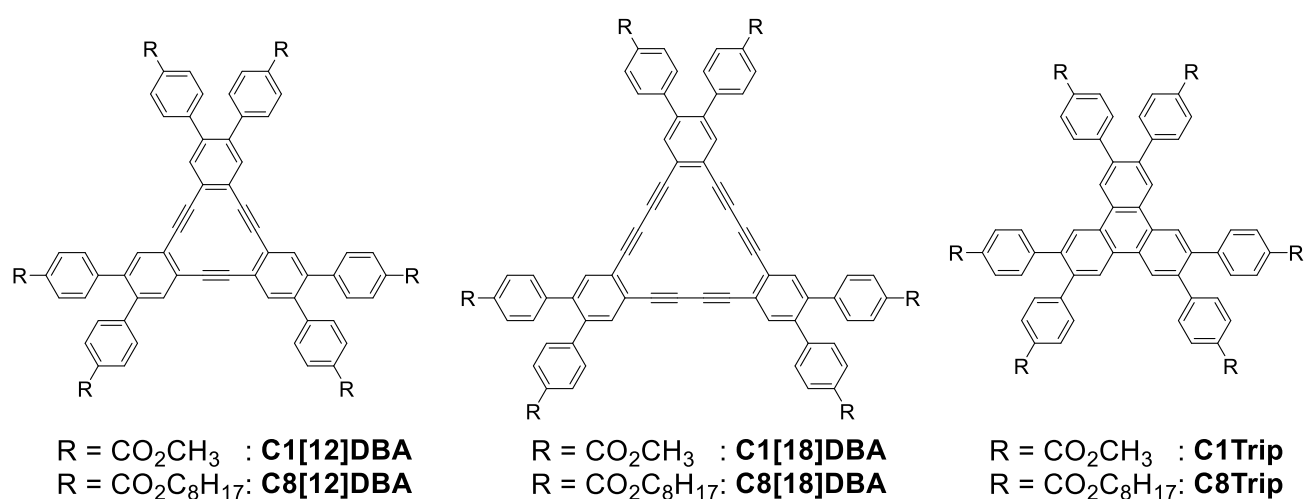
To date, molecular glasses based on designs incorporating molecular shape, structural flexibility, and intermolecular interactions have been reported, including starburst-type molecules developed by Shirota et al.,^{12,13} propellane skeletons, camphorsulfonamides, pillararene, and cholesteryl group-substituted carbazole derivatives.^{21–28} In molecules capable of forming both crystalline and glassy phases, chromic phenomena and polarization properties associated with changes in molecular arrangement have been observed, and the relationship between phase transition behavior and intermolecular interactions has been discussed.^{23,26–28} We have discovered that rod-shaped dumbbell molecules linked with camphorsulfonamide and adamantylamine undergo a transition from a liquid to a plastic crystal and then to an orientational glass.²⁵ In such systems, the correlation between intermolecular interactions and dielectric relaxation, chromic behavior, and luminescence properties can be discussed at the molecular level. However, due to the non-equilibrium nature and structural disorder of molecular glasses, it is difficult to understand intermolecular interactions using methods such as X-ray crystallographic analysis.

Symmetrical polyaromatic hydrocarbons (PAHs) such as porphyrin, pyrene, perylene, and pentacene tend to form crystalline molecular assemblies via π -stacking columns and multiple C–H $\cdots\pi$

interactions, and do not form a glass state.^{29,30} C_3 -symmetric hexadehydrotribenzo[12]annulene (**[12]DBA**), where three phenylene groups are bridged by ethynyl groups ($-C\equiv C-$), has a pore at the molecular center, resulting in limited intermolecular interaction, and thus is expected to exhibit intermolecular interactions different from those of symmetric PAHs.^{31,32} Additionally, **[12]DBA** exhibits distinctive physical properties in terms of optical characteristics, aromaticity, redox properties, and single-molecule conductivity, and is known to exhibit luminescence behavior with a large Stokes shift.^{33–40} The molecular assembly structures of **[12]DBA** derivatives change dramatically depending on the position and type of substituents. Unsubstituted **[12]DBA** forms a herringbone packing structure due to multiple $C-H\cdots\pi$ interactions,⁴¹ whereas introducing substituents such as carboxyl groups at the 2, 6, 10-positions or 2, 3, 6, 7, 10, 11-positions, diverse crystalline structures with varying dimensionalities emerge, including one-dimensional (1D) columns,^{42–44} two-dimensional (2D) layers,^{43,45–47} three-dimensional (3D) tetrahedral structures,⁴³ and isolated dimers.^{22,48} Additionally, the formation of 1D columnar liquid crystals⁴⁹ and nanostructures^{38,39,50–52} has also been reported.

We reported molecular glass based on **[12]DBA** with bulky octylbenzoate groups at 2,3,6,7,10,11-position (**C8[12]DBA** in Scheme 1).²² **[12]DBA** derivatives with phenylcarboxyl and methylbenzoate groups form crystalline states made up of HOF and π -stacked dimer structures through hydrogen-bonding and π -stack interactions. These crystals cause a red-shift in the absorption spectrum because of strong π - π interactions. On the other hands, the intermolecular π - π interactions of **C8[12]DBA** were weakened due to steric hindrance of the phenylene units and thermal fluctuation of octyl-ester chains, inhibiting crystallization, and **C8[12]DBA** exhibited isolated-molecule-like luminescence behavior and dielectric relaxation phenomena caused by thermal fluctuations in the alkyl ester chains in the solid state. This result provides a new design strategy for π -molecular-based glass materials. However, many details regarding the intermolecular interactions contributing to the formation of the glass phase and their dynamics remain unclear.

In dehydrobenzoannulene (**DBA**) derivatives, the ring size can be controlled by designing the synthetic precursor.^{53,54} Iyoda, Diederich, Haley, Goodson, Komatsu, and others have shown the redox properties and optical properties of **DBA** derivatives with various ring sizes.^{33,37–39,53,55,56} Furthermore, Tahara, Tobe, De Feyter, and others have reported the formation of nanostructures on substrate surfaces and the intermolecular fastener effect of alkoxy-substituted **DBA** derivatives.^{50,57} Hisaki et al. have reported on the formation of HOF materials based on π -expanded DBA derivatives and their gas adsorption behavior.^{45–47,58–60} By understanding the correlation between the ring size of **DBA** derivatives and their molecular assembly structures, the design strategy for molecular glasses of **DBA** derivatives can be clarified. In this study, we synthesized **[18]DBA** derivatives (**C8[18]DBA** in Scheme 1) formed by more elongated $-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$ bonds with larger central pore and the corresponding smaller triphenylene derivative without pore structure (**C8Trip** in Scheme 1), and compared their phase transition behavior, molecular assembly structures, dielectric, and optical properties with **C8[12]DBA**. Additionally, single-crystal X-ray structural analyses of the corresponding methylbenzoate derivatives (**C1[12]DBA**, **C1[18]DBA**, and **C1Trip** in Scheme 1) were performed to evaluate the molecular arrangement patterns in the π -cores.



Scheme 1. Chemical structures of **C8[n]DBA**, **C1[n]DBA** ($n = 12$ or 18), **C1Trip** and **C8Trip**.

2. Experimental Section

General. Solution phase ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker Avance III 400 or a JEOL JNM-ECZ400S NMR spectrometer. Chemical shifts (δ) are expressed in ppm with reference to tetramethylsilane (^1H 0.00 ppm) or residual nondeuterated solvent (CDCl_3 ; ^{13}C 77.0 ppm) as an internal standard. Mass spectra were recorded on a JMS-700 spectrometer at the NMR and MS Laboratory, Graduate School of Engineering, Tohoku University. Elemental analyses were performed on a Microcoder JM10 at the Elementary Analysis Laboratory, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University. IR spectra were measured on a Thermo Scientific NICOLET 6700 FT-IR spectrometer. Thermogravimetric (TG) analysis was performed on a Rigaku Thermoplus EVO-2 at a scan rate of 10 K/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis was conducted using a Mettler Toledo DSC-1 at a scan rate of 10 K/min. Microscopic observations were made using a Nikon ECLIPSE LV100ND, and stereomicroscopic and polarized light micrographs were taken using a Canon EOS kiss x5. The measurement sample was a powdered sample placed on a glass slide and sandwiched between cover glasses. Temperature control was performed by placing the sample on a temperature control stage (Linkam Scientific LTS-E350) to observe the sample and check its fluidity. Temperature-dependent powder X-ray diffraction (PXRD) patterns and were collected by using a Rigaku Ultima III diffractometer with Cu Ka radiation at $\lambda = 1.54187 \text{ \AA}$. UV-vis absorption spectrum was measured on Perkin Elmer LAMBDA 750A Spectrometer. Fluorescent spectrum was measured on Shimadzu RF-6000. The fluorescence quantum yield in solution was determined using a SHIMADZU integrating sphere. For UV-vis spectra of solids, samples and KBr powder were mixed in an agate mortar, and pellets with a diameter of 13 mm were prepared by a pressure-molding machine and measured in the transmission configuration. Temperature-dependent dielectric constants of the compounds were measured using a four-probe AC impedance method at a frequency range of 1 kHz to 1 MHz (Hewlett-Packard, S4 HP4194A) with a liquid crystal cell in a Linkam LTS350 temperature-control system.

Powder of **C8Trip** and **C8[18]DBA** were fabricated on indium tin oxide (ITO) glass (SZ-A311P6N), which were sandwiched by a corresponding ITO glass to form a dielectric measurement cell with an electrode area of 0.16 cm². The average electrode gap of **C8Trip** and **C8[18]DBA** was 115 μ m and 30 μ m, respectively.

Fluorescence Lifetime Measurements. Fluorescence lifetimes were measured by a Horiba FluoroCube time-correlated single-photon-counting (TCSPC) system equipped with a TBX picosecond photon detection module (Figure S1). The samples were excited at 279 nm or 375 nm using pulse laser sources (Horiba PicoBrite series). Filters were used to minimize the scattered light at the excitation wavelength. The instrumental response (IRF) was recorded using a LUDOX HS-30 colloidal silica suspension in water (Aldrich). The simulation of decay profiles was performed by a nonlinear least-squares method.

Preparation of C8Trip. Preparation of compound **1** was performed according to the procedure of previous report (Scheme S1).⁵⁹ A solution of **1** (2.00 g, 2.18 mmol) in SOCl₂ (80 mL) was refluxed for 15 h. The reaction mixture was evaporated to dryness under reduced pressure. The yellow residue was dissolved in dry dichloromethane (80 mL), and then, anhydrous triethylamine (2.34 μ L, 16.9 mmol) and 1-octanol (2.34 mL, 14.8 mmol) was added. The resulting mixture was stirred at room temperature for 25 h, then quenched with water and extracted with dichloromethane. The combined organic layer was washed with water and brine and then dried over MgSO₄. After evaporation of solvent under reduced pressure, the crude product was purified by silica gel column chromatography (CHCl₃), affording **C8Trip** (1.72 g) as a white amorphous solid in 50% yield. ¹H NMR (400 MHz, CDCl₃): δ = 8.72 (s, 6 H), 7.98 (d, J = 8.3 Hz, 12 H), 7.39 (d, J = 8.3 Hz, 12 H), 4.32 (t, J = 6.7 Hz, 12 H), 1.77 (quint, J = 7.1 Hz, 12 H), 1.49 – 1.20 (m, 60 H), 0.89 (t, J = 6.9 Hz, 18 H); ¹³C NMR (100 MHz, CDCl₃): 166.4, 145.4, 139.4, 130.0, 129.5, 129.3, 129.2, 125.8, 65.3, 31.8, 29.2, 29.3, 28.7, 26.0, 22.6, 14.1; MS: calc. 1620.9719, found 1620.9718. E.A. Calc. for C₁₀₈H₁₃₂O₁₂, C, 79.96 %; H, 8.20 %; N, 0.00 %; found C, 80.14 %; H, 8.50 %; N 0.15%.

Preparation of C8[18]DBA. C8[18]DBA was prepared by following Scheme S2. Preparation of compound **5** and **6** were performed according to the procedure of previous reports.^{60, 61}

Preparation of 3. To a mixture of 4-boronobenzoic acid **2** (17.3 g, 104 mmol), K₂CO₃ (36.2 g, 262 mmol) in dry DMF was added 1-bromooctane (50 mL, 287 mmol). The mixture was stirred at 90 °C for 48 h. After cooling to room temperature, 3M H₂SO₄ aq. was added to the reaction mixture until the resulting bubble stopped. The mixture was extracted with ethyl acetate. The combined organic layer was washed with 2M LiCl aq., water and brine, then dried over MgSO₄. After evaporation of the solvent under reduced pressure, the crude product was purified by silica gel column chromatography (hexane / ethyl acetate = 1/0→1/2) to give the mixture of **3** and unidentified impurity as a white solid (19.1 g). The following reaction was performed without further purification. ¹H NMR (400 MHz, CDCl₃): δ = 8.29 (d, J = 8.4 Hz, 2H), 8.16 (d, J = 8.3 Hz, 2H), 4.37 (t, J = 6.7 Hz, 2H), 1.81 (quint, J = 7.1 Hz, 2 H), 1.51-1.29 (m, 10 H), 0.90 (t, J = 7.2 Hz, 3H).

Preparation of 7. Compound **3** (19.1 g, 68.7 mmol) and **6** (20.1 g, 33.7 mmol) were dissolved in mixed solvent of toluene (340 mL), water (170 mL) and 1,4-dioxane (170 mL). The solution was degassed with N₂ bubbling. K₂CO₃ (7.14 g, 67.4 mmol), followed by Pd(dppf)Cl₂ (2.42 g, 3.31 mmol) was added to the solution. The mixture was refluxed for 48 h. After cooling to room temperature, the resulting mixture was concentrated *in vacuo* and then extracted with ethyl acetate. The combined organic layer was washed with water and brine, then dried over MgSO₄. After evaporation of the solvent under reduced pressure, the crude product was purified by twice silica gel column chromatography (eluent for first column chromatography: CH₂Cl₂, eluent for 2nd column chromatography: toluene / hexane = 1/1) to give the **7** as yellow oil (17.9 g, 69 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.87 (d, 4H, J = 8.4 Hz), 7.56 (s, 2H), 7.15 (d, 4H, J = 8.8 Hz), 4.29 (t, J = 6.7 Hz, 4 H), 1.74 (quint. J = 7.0 Hz, 4H), 1.28-1.46 (m, 20H), 1.14 (s, 42H), 0.89 (t, J = 6.8 Hz, 6H).

Preparation of 8. To a solution of **7** (17.9 g, 19.8 mmol) in THF was added 1 M TBAF THF soln. (46.8 mL, 46.8 mmol). The reaction mixture was stirred for 1h at room temperature. The reaction was

quenched with water, then the resulting mixture was extracted with CHCl_3 . The combined organic layer was washed with water and brine, dried over MgSO_4 . After evaporation of the solvent under reduced pressure, the crude product was purified by silica gel column chromatography (toluene / $\text{CHCl}_3 = 1/0 \rightarrow 0/1$) to give the mixture of **8** as a dark purple oil (9.76 g, 83%). The following reaction was performed without further purification due to instability of the product. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.89$ (d, 4H, $J = 8.8$ Hz), 7.61 (s, 2H), 7.16 (d, 4H, $J = 8.8$ Hz), 4.29 (t, $J = 6.7$ Hz, 4 H), 3.41 (s, 2H), 1.74 (quint. $J = 7.0$ Hz, 4H), 1.28-1.46 (m, 20H), 1.14 (s, 42H), 0.89 (t, $J = 6.8$ Hz, 6H).

Preparation of C8[18]DBA. Copper diacetate (II) (11.3 g, 62.3 mmol) was dissolved in MeOH (400 mL), pyridine (400 mL) and diethyl ether (80 mL). A solution of **8** (9.76 g, 16.5 mmol) in mixed solvent of pyridine (160 mL) and MeOH (160 mL) was added dropwise to the solution over a period of 2 h with a dropping funnel. The mixture was stirred for 0.5 h at 60 °C and the 22 h at room temperature under air. After the filtration of the reaction mixture, the black solution was concentrated *in vacuo*. The crude product was passed through the silica gel short path column (AcOEt), and then purified by silica gel column chromatography (toluene / CHCl_3 , 0% $\rightarrow$ 100% of CHCl_3) and GPC (CHCl_3) to give **C8[18]DBA** as a brown waxy solid (1.23 g, 13 %). The waxy solid was suspended in EtOH and the insoluble material was centrifuged and washed with EtOH to give brown solid of **C8[18]DBA** (1.19 g). ^1H NMR (400 MHz, CDCl_3): δ 7.93 (d, 12H, $J = 8.0$ Hz), 7.78 (s, 6H), 7.21 (d, 12H, $J = 8.4$ Hz), 4.29 (t, $J = 6.7$ Hz, 12 H), 1.74 (quint. $J = 7.0$ Hz, 12H), 1.28-1.46 (m, 60H), 0.89 (t, $J = 6.8$ Hz, 18H); ^{13}C NMR (100 MHz, CDCl_3): 166.2, 143.7, 140.5, 134.7, 129.7, 129.6, 124.9, 80.7, 79.0, 65.3, 31.8, 29.2, 29.1, 28.7, 26.0, 22.6, 14.1; MS: calc. 1764.9719, found 1764.9718, E.A. Calc. for $\text{C}_{120}\text{H}_{132}\text{O}_{12}$, C, 81.60 %; H, 7.53 %; N, 0.00 %. Found. C, 81.66 %; H, 7.53 %; N, 0.00 %.

Single crystal structure X-ray structural analysis of C1Trip. Single crystals of **C1Trip** were obtained using a slow cooling method of the 1,4-dioxane. Crystallographic data were collected using a Rigaku RAPID-II diffractometer equipped with a rotating anode fitted with a multilayer confocal optics and using Cu $\text{K}\alpha$ ($\lambda = 1.54187 \text{ \AA}$) radiation from a graphite monochromator (Table 1). Structural

refinements were performed using the full-matrix least squares method on F^2 . The initial structure was solved using SHELXT,⁶² and structural refinement was performed using OLEX2 software and SHELXL.^{63, 64} All the parameters, except for those of the hydrogen atoms, were refined using anisotropic temperature factors.

Table 1. Crystal data, data collection, and reduction parameters for C1[*n*]DBA and C1Trip.^{22, 60}

Crystal	C1[12]DBA ²²	C1[18]DBA ⁶⁰	C1Trip
<i>Chemical formula</i>	C ₇₂ H ₄₈ O ₁₂ (C ₇ H ₈)	C ₇₈ H ₄₈ O ₁₂ 2(C ₄ H ₈ O ₂)	C ₆₆ H ₄₈ O ₁₂ 5(C ₄ H ₈ O ₂)
<i>Formula weight</i>	1197.23	1353.44	1473.56
<i>T, K</i>	100	153	120
<i>Space group</i>	<i>P2₁/n</i>	<i>P2₁/c</i>	<i>I2/a</i>
<i>a, Å</i>	24.3648(9)	16.9723(2)	30.7338(8)
<i>b, Å</i>	9.5585(4)	11.80850(10)	26.7298(7)
<i>c, Å</i>	25.8540(10)	34.2230(5)	37.202(5)
<i>β, deg</i>	94.315(7)	93.9459(5)	101.889(8)
<i>V, Å³</i>	6004.1(4)	1575.27(7)	29906(4)
<i>Z</i>	4	4	16
<i>D_{calc}, g·cm⁻³</i>	1.324	1.314	1.309
<i>μ, cm⁻¹</i>	7.19	—	7.75
<i>Reflections measured</i>	61595	40881	165054
<i>Independent reflections</i>	9541	14813	27278
<i>Reflections used</i>	9541	14813	27278
<i>R_{int}</i>	0.1237	0.056	0.0927
<i>R₁^a</i>	0.0973	0.0771	0.0876
<i>R_{all}</i>	0.1689	—	0.1360

$R_w(F_2)^a$	0.2507	0.2381	0.2493
GOF	1.033	1.036	1.018
CCDC	2069905	1035274	2455080

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $R_w = (\Sigma \omega(|F_o| - |F_c|)^2 / \Sigma \omega F_o^2)^{1/2}$.

Theoretical calculation. DFT calculations were performed with the Gaussian 16 program package.⁶⁵ The optimized molecular structures of **C1Trip**, **C1[12]DBA**, and **C1[18]DBA** were obtained by DFT calculations with the B3LYP/6-31G(d,p) basis set. The stationary point was assessed by a vibration frequency analysis. On the calculations to estimate the interaction energies between intra/inter dimer with counterpoise correction, we used the B3LYP functional and the 6-31G basis set. Van der Waals corrections are calculated based on DFT-D3 method with Becke–Jonson damping.⁶⁶ The experimental crystal structure at 100 K was used as the dimer structure (Figures S2, 3). These structures were optimized with freezing all atoms except for hydrogen atoms. The intermolecular interaction energy in a dimer (E_{intra}), defined as the difference between the energy of dimer A-B and the sum of the energies of monomers A and B, was calculated using equation (1).

$$E_{\text{intra}} = E(\text{dimer A-B}) - [E(\text{monomer A}) + E(\text{monomer B})] \quad (1)$$

$$E_{\text{inter}} = E(\text{tetramer, A-A} \sim \text{B-B}) - [E(\text{dimer, A-A}) + E(\text{dimer, B-B})] \quad (2)$$

Additionally, to estimate only the influence of the π -electron core, molecular interaction energies within dimers (E_{intra}^{π}) and between dimers (E_{inter}^{π}) were calculated using equations (1) and (2) with molecular structures excluding the methyl benzoate group (Figure S4).

3. Results and Discussion

3.1. Preparation and electronic structures of C8[*n*]DBA and C8Trip. Preparation of **C8[18]DBA** and **C8Trip** were summarized in Schemes S1 and S2. **C8Trip** was synthesized by six-fold esterification of 1-octanol and the corresponding carboxylic acid with 50% yield (Scheme S1). **C8[18]DBA** was synthesized by cyclotrimerization of the corresponding diethynyl *o*-terphenyl with octylester groups (Scheme S2). The optimized molecular structure and electronic states of **C1[*n*]DBA** and **C1Trip** were calculated using DFT calculations with B3LYP/6-31G(d,p) basis set (Figures S5–7). The HOMO and LUMO of **C1[12]DBA** were -5.48 and -2.54 eV, respectively, and their orbital extended across the entire **[12]DBA** molecule with threefold symmetry (Figure S5). On the other hand, the HOMO and LUMO of **C1[18]DBA** exhibited pseudo-double degeneracy with energy levels of -5.70 and -2.48 eV, respectively. The frontier orbitals were localized at one vertex of the **[18]DBA** π -core and its opposite edge, and the three-fold symmetry of the electronic structure was broken (Figure S6). This difference in the electronic structures between **C1[12]DBA** and **C1[18]DBA** is attributed to the difference in Hückel's aromaticity.⁶⁷ The HOMO and LUMO of **C1Trip** were observed at -5.98 and -1.95 eV, respectively, showing similar electronic states to **C1[18]DBA** (Figure S7), and π -orbitals were distributed also on the phenylene units. This difference in electronic structures is considered to influence intermolecular interactions.

3.2. Thermal properties of C8[*n*]DBA and C8Trip. Thermogravimetry (TG) measurements of **C8[18]DBA**, **C8[12]DBA**, and **C8Trip** showed thermal decomposition accompanied by weight-loss at around 580, 540, and 600 K, respectively (Figure S8). Figure 1a shows the DSC curves for **C8[18]DBA**, **C8[12]DBA**, and **C8Trip**. The as-grown brown powder sample of **C8[18]DBA** obtained by recrystallization turned black waxy solid at around 440 K, which is approximately 150 K lower than the thermal decomposition temperature observed in the TG chart (Figures 1b, c). Powder X-ray diffraction (PXRD) pattern of the black waxy solid showed a broadening of the diffraction pattern and sharp peak at $2\theta = 3.04^\circ$ also changed to the broad peak (Figure S9), suggesting the formation of

amorphous solid after the thermal polymerization of **C8[18]DBA**. The differential scanning calorimetry (DSC) curve shows an irreversible phase transition at 350 K from the low-temperature phase (LTP) to high-temperature phase (HTP), and showed a small endothermic peak around 440 K, followed immediately by a large exothermic peak with $\Delta H = -429 \text{ kJ mol}^{-1}$ (Figure 1a). This ΔH value is approximately three times that of the polymerization of a single $-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$ (-130 to -160 kJ mol^{-1}),⁶⁸ suggesting that the three $-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$ units within the molecule underwent quantitative thermal polymerization. On the other hand, no similar thermal polymerization reaction was observed in **C8[12]DBA**, which has a $-\text{C}\equiv\text{C}-$ structure. The thermal stability of **C8[n]DBA** derivatives and **C8Trip** decreased in the order **C8Trip** > **C8[12]DBA** > **C8[18]DBA**.

C8[18]DBA does not exhibit phase transitions below the thermal polymerization temperature, whereas **C8[12]DBA** showed a characteristic DSC baseline change at approximately 320 K during the cooling process from the liquid state, indicative of a glass (G) transition (Figure 1a, Figure S10, Table S1). This phase transition was a reversible phase transition without supercooling during the thermal cycle. On the other hand, **C8Trip** exhibited a reversible endothermic peak at 450 K ($\Delta H = 20.2 \text{ kJ mol}^{-1}$, $\Delta S = 44.9 \text{ J K}^{-1} \text{ mol}^{-1}$; Figure 1a and Table S1), and polarized optical microscopy (POM) observations under cross-Nicole optical arrangement confirmed that this was a solid-liquid phase transition (Figure 1c). These results indicate that even when the structural units at the molecular ends are identical, differences in the molecular center unit can significantly alter phase transition behavior and intermolecular interactions. Notably, the glass transition temperature of **C8[12]DBA** (320 K) is more than 100 K lower than the melting point of **C8Trip** (450 K) and the polymerization point of **C8[18]DBA** (440 K), corresponding to weaker intermolecular interactions between **C8[12]DBA** molecules in the glass state.

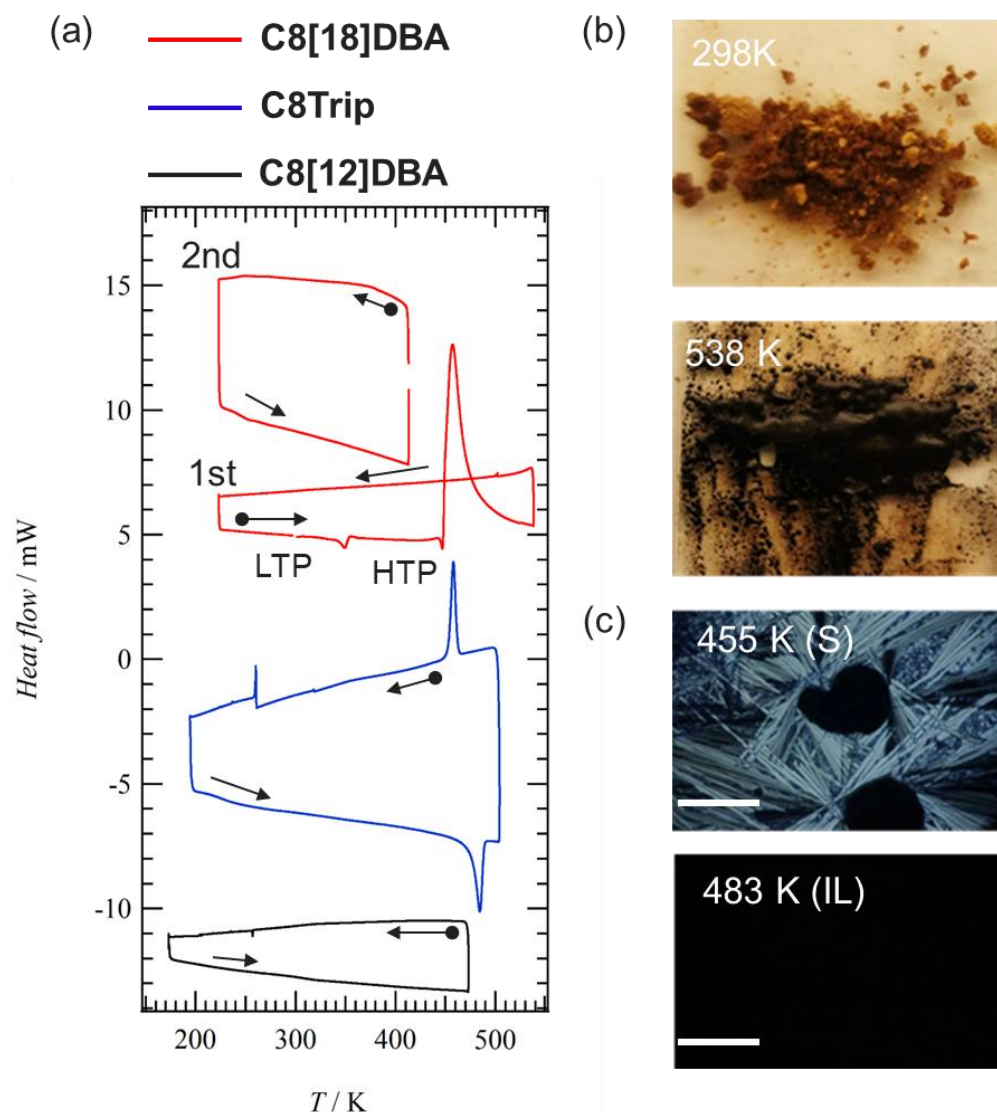


Figure 1. Thermal behavior and phase transition of **C8[*n*]DBA** and **C8Trip**. (a) DSC curves of **C8[18]DBA** (red line with 1st and 2nd scans), **C8Trip** (blue line), and **C8[12]DBA** (black line). (b) Images of as-grown **C8[18]DBA** powder at 298 K (top) and 538 K (bottom). (c) POM images of the solid phase of **C8Trip** at 455 K (top) and the isotropic liquid phase at 483 K (bottom). The scale bar is 300 μm .

3.3. π -Stacking interaction of C1[*n*]DBA and C1Trip. The intermolecular interactions between the π -cores were evaluated based on single-crystal X-ray structural analyses of **C1[*n*]DBA** derivatives and **C1Trip** with methyl ester groups. The **C1[12]DBA** crystal contained one toluene as the crystallization

solvent. The annulenes at the molecular center maintained a π -planar structure, and the terminal phenyl groups were tilted at a dihedral angle (ϕ) of 45–74° relative to the π -core (Figure 2a and Figure S11a), forming a conformation that reduced steric hindrance between adjacent phenylene units. **C1[12]DBA** formed π -dimers rotated 180° relative to each other, which formed a 1D column by shifting the π -plane along the b -axis (Figure 2a). The average distance between annulene π -planes within the π -dimer was 3.35 Å, shorter than the sum of van der Waals radii of carbon atoms (3.4 Å), indicating weak π - π interactions between acetylene units (Figures 2a, b). On the other hand, the average distance between annulene π -dimers was 3.92 Å, which was 0.6 Å longer than that within dimers, indicating that intermolecular interactions between π -dimers were negligible.

The $\phi = 36.5$ –57.4° in **C1[18]DBA** is smaller than that of **C1[12]DBA** (Figure 2b, Figure S11b). This is due to the reduction of intermolecular steric hindrance between phenylene units in the π -dimer as the molecular size increases. **C1[18]DBA** forms a slip-stacked type π -dimer with a large π -plane shift, forming a 1D column along the b -axis while minimizing steric hindrance at the terminal phenylene groups (Figure 2b). The average distance between the annulene planes of intra π -dimer and inter π -dimers was 3.28 Å for both, indicating significant π - π interactions despite the significant slip of the π -plane.

The $\phi = 46$ –54° in **C1Trip** was similar to those of **C1[12]DBA** (Figure S11c). **C1Trip** formed a slip-stacked π -dimer with a significantly shifted π -plane, forming a non-uniform 1D column along the b -axis (Figure 2c). However, the average interplanar distances between the triphenylene units for intradimer and interdimer were 4.53 and 4.72 Å, respectively, and no significant intermolecular π - π interactions were observed due to severe steric hindrance at the terminal phenylene units. It was clarified that even when the structure of the terminal phenylene units is the same, intermolecular interactions within the π -dimer and between π -dimers can vary significantly depending on the size of the molecular structure.

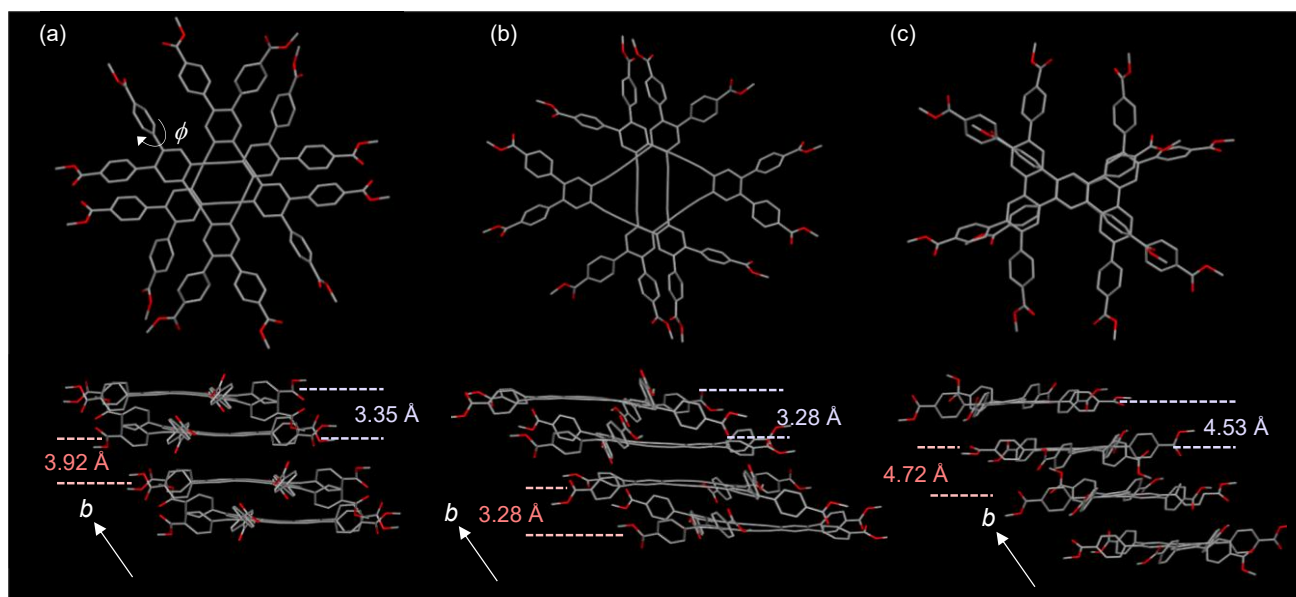


Figure 2. π -stacking interactions between **C1[n]DBAs** and **C1Trip**. (a) **C1[12]DBA**, (b) **C1[18]DBA**, and (c) **C1Trip** forming π -dimers in a one-dimensional column (top) and the average interplanar distance between annulene units (bottom). Intradimer and interdimer distances are shown in blue and red, respectively.

3.4. Molecular assembly structures of C8[n]DBA and C1Trip. **C8[n]DBAs** and **C8Trip** could not be obtained as single crystals, so their molecular assembly structures are discussed based on PXRD patterns. The temperature-dependent PXRD patterns of **C8[12]DBA** show only weak, broad reflections in both the LTP and the HTP, which is characteristic of a glass state in which the periodicity of molecular position disappeared (Figure 3a). On the other hand, the PXRD pattern of **C8[18]DBA** at 373 K shows a diffraction peak corresponding to a hexagonal lattice with $a = 28.3$ Å, suggesting that the molecular π -core is arranged in a hexagonal pattern within the ab plane (Figure 3a, red line, and Table S2). Concurrently, a broad reflection appears around $2\theta \sim 20^\circ$, suggesting a random state where the alkyl chains are disordered. The theoretical maximum molecular length for **C8[18]DBA** when the terminal alkyl chains adopt an all-*trans* conformation is 45 Å (Figure 3b), which is more than 16 Å longer than the observed length of the a -axis (28.3 Å). Therefore, the alkyl chains of **C8[18]DBA** are considered to be interdigitated in a random conformation. This molecular assembly structure is

similar to the discotic hexagonal columnar (Col_h) liquid crystal phase. However, **C8[18]DBA** does not exhibit a phase transition to the liquid crystal phase, where the thermal mobility of the molecular π -cores required for liquid crystal formation is not realized. Furthermore, reflection peaks that cannot be attributed to the Col_h liquid crystal phase were observed at $2\theta = 7.74$ and 14.8° (Figure 3a, red line). The correlation lengths of these peaks were $d = 11.4$ and 5.99 Å, respectively, with a ratio of 1:2. The former peak at $d = 11.4$ Å is in good agreement with $b = 11.80850(10)$ Å from the single-crystal X-ray structural analysis of **C1[18]DBA** (Figure 2a) and can be attributed to a peak reflecting the uniform dimerized π -stacking column.

The PXRD pattern of **C8Trip** at 298 K shows a reflection peak corresponding to a periodic structure with $d_{100} = 22.6$ Å at $2\theta = 3.93^\circ$, and a peak corresponding to 200 reflections at $2\theta = 7.90^\circ$ (Figure 3a, blue line, and Table S3), and a broad reflection peak appears around $2\theta \sim 20^\circ$. The maximum molecular length of **C8Trip** when the alkyl chains adopt an all-trans conformation is estimated to be 39 Å (Figure 3b), which is approximately 16 Å longer than the measured $d_{100} = 22.6$ Å. Therefore, it is considered that the alkyl chains adopt a random conformation in which they interdigitate with each other. Additionally, a peak corresponding to $d = 14.0$ Å was observed at $2\theta = 6.30^\circ$ (Figure 3a, blue line), which is a half the value of $b = 26.7298(7)$ Å from the single-crystal structure analysis of **C1Trip** (Figure 2c). Therefore, these peaks can be attributed to the periodicity of the non-uniform π -dimerized column along the b -axis. The molecular assembly structure of **C8Trip** is a 1D columnar structure composed of π -dimers, similar to **C8[18]DBA**, its crystallinity was reduced compared to **C8[18]DBA** due to weaker intermolecular interactions (Figure 3c). Although three compounds of **C8[12]DBA**, **C8[18]DBA**, and **C8Trip** have similar terminal substituents, their crystallinities differed from one another.

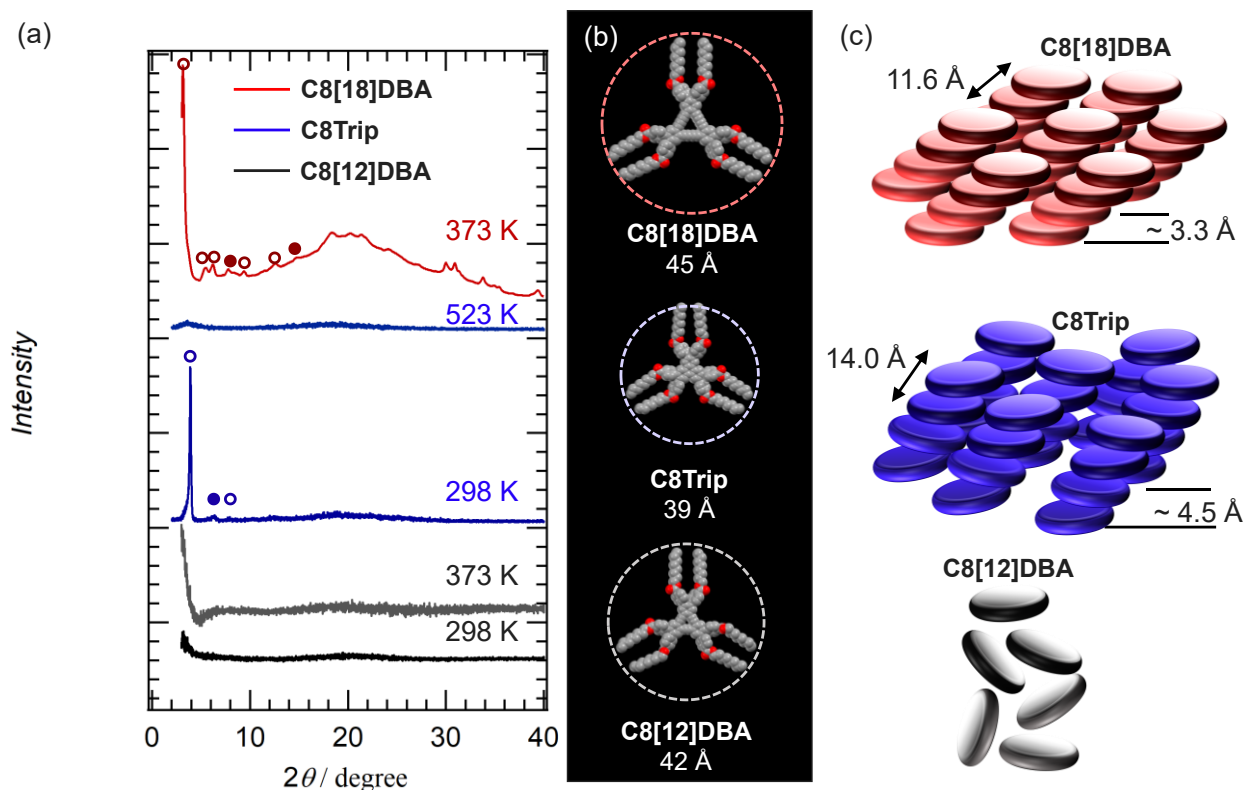


Figure 3. Molecular assembly structure of **C8[n]DBAs** and **C8Trip**. (a) Temperature-dependent PXRD patterns of **C8[18]DBA** (red line), **C8Trip** (blue line), and **C8[12]DBA** (black line). The open circles in the figure indicate peaks attributable to the intermolecular spacing between the π -cores, and the filled circles represent peaks attributable to the periodicity in the π -dimerized column. (b) Model structures and maximum molecular lengths of **C8[18]DBA**, **C8Trip**, and **C8[12]DBA**, adopting the all-trans conformation of alkyl chains based on DFT calculation. (c) Schematic representations of the columnar structures of **C8[18]DBA**, **C8Trip**, and **C8[12]DBA**.

3.5. Intermolecular interaction energy. To quantitatively evaluate the intermolecular interactions between the π -cores of **C8[n]DBA** and **C8Trip**, the stabilization energies of intradimer (E_{intra}) and interdimer (E_{inter}) were calculated using the DFT-D method (B3LYP/6-31G and GD3BJ) based on the crystal structure of **C1[n]DBA** and **C1Trip**, and the counterpoise correction was applied (Figure 4a, Table 2, and Figures S2, 3). Furthermore, the interaction energies of the π -core structures of **[12]DBA**,

[18]DBA, and **Trip**, which have had their terminal phenylene units removed, were also calculated using the same method as E_{intra}^{π} and E_{inter}^{π} (Figure 4b, Table 2, and Figure S4).

The E_{intra} changes in the order of **C1[12]DBA** ($-58.8 \text{ kcal mol}^{-1}$) > **C1[18]DBA** ($-42.8 \text{ kcal mol}^{-1}$) > **C1Trip** ($-35.7 \text{ kcal mol}^{-1}$), with **C1[12]DBA** having the largest stabilization energy. On the other hand, the E_{intra}^{π} for the π -core alone was in the order of **[12]DBA** ($-17.1 \text{ kcal mol}^{-1}$) > **[18]DBA** ($-15.8 \text{ kcal mol}^{-1}$) >> **Trip** ($-2.69 \text{ kcal mol}^{-1}$), indicating that the intermolecular interaction for π -dimer formation in **Trip** was significantly smaller. The E_{inter} varied in the order **C1[18]DBA** ($-51.5 \text{ kcal mol}^{-1}$) > **C1[12]DBA** ($-46.9 \text{ kcal mol}^{-1}$) > **C1Trip** ($-39.6 \text{ kcal mol}^{-1}$), showing a different trend from the sequence of interactions within the π -dimer. The E_{inter}^{π} of the π -core alone also showed a similar trend to E_{inter} , with **[18]DBA** ($-11.2 \text{ kcal mol}^{-1}$) >> **[12]DBA** ($-6.52 \text{ kcal mol}^{-1}$) > **Trip** ($-2.76 \text{ kcal mol}^{-1}$). From a comparison of the absolute values of E_{inter} and E_{inter}^{π} , the contribution of intermolecular interactions originating from the annulene π -core at the molecular center in **C1[n]DBA** was relatively small, and interactions between the phenylene units at the molecular ends contributed more to overall stabilization. Although the value of $E_{\text{intra}} + E_{\text{inter}}$ was the highest in **C1[12]DBA**, the crystallinity of **C8[12]DBA** was lower than that of **C8[18]DBA** or **C8Trip**. Therefore, it was found that the magnitude of intermolecular interaction energy is not necessarily related to crystallinity. In **C1[18]DBA** and **C1Trip**, there was no significant difference between the intermolecular interaction energy of E_{intra} and E_{inter} , and the difference of these interactions was relatively small. On the other hand, **C1[12]DBA** forms strong π -dimers, however, the intermolecular interactions are unbalanced, leading to random packing between π -dimers and the formation of a molecular glass.

Table 2. Intermolecular interaction energies within dimers (E_{intra}) and between dimers (E_{inter}) of C1[18]DBA, C1Trip, and C1[12]DBA, and the effect of π -electron cores (E_{intra}^{π} and E_{inter}^{π}).^a

Compounds	C1[18]DBA	C1Trip	C1[12]DBA
$E_{\text{intra}} / \text{kcal mol}^{-1}$	−42.8	−35.7	−58.8
$E_{\text{inter}} / \text{kcal mol}^{-1}$	−51.5	−39.6	−46.9
Compounds	[18]DBA	Trip	[12]DBA
$E_{\text{intra}}^{\pi} / \text{kcal mol}^{-1}$	−15.8	−2.69	−17.1
$E_{\text{inter}}^{\pi} / \text{kcal mol}^{-1}$	−11.2	−2.76	−6.52

^a Calculated by B3LYP / 6–31G GD3BJ and counterpoise method.

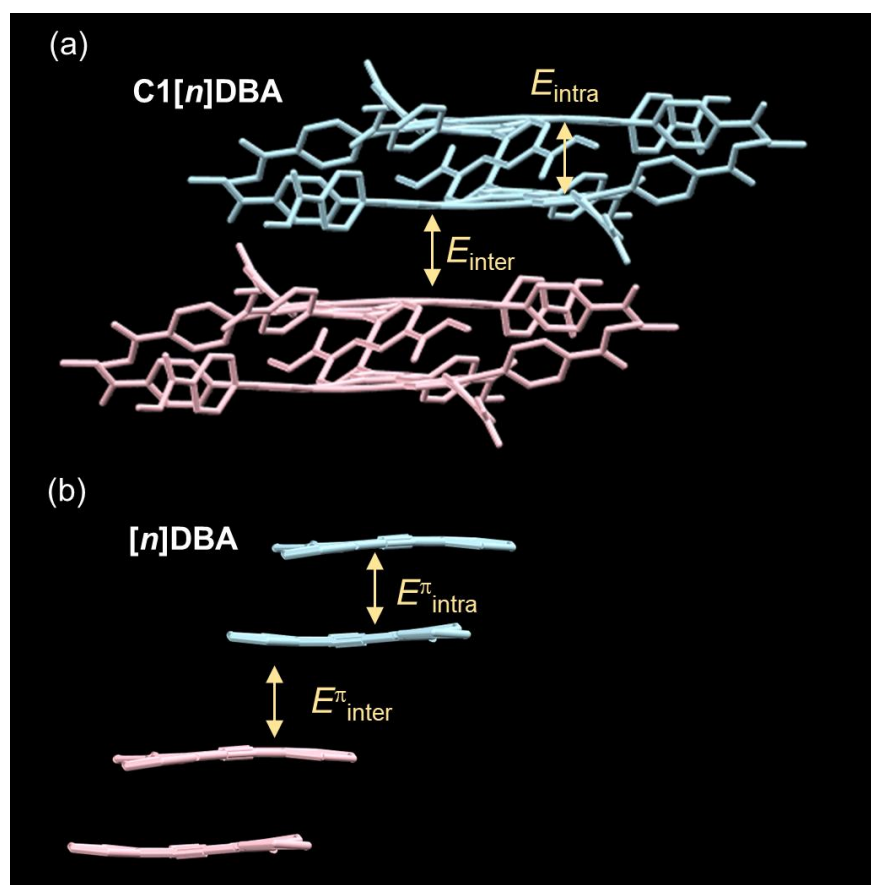


Figure 4. Intermolecular interaction energies within and between π -dimers in single crystals of C1[n]DBA. (a) Intradimer interactions (E_{intra}) and interdimer interactions (E_{inter}) in C1[n]DBA and

C1Trip. (b) Intradimer interactions (E_{intra}^{π}) and interdimer interactions (E_{inter}^{π}) within π -dimers of **[*n*]DBA**, calculated excluding the phenylene moieties at the molecular ends.

3.6. Dielectric properties and molecular dynamics. To evaluate the dynamics of **C8[*n*]DBA** and **C8Trip**, the variable frequency (f) and temperature (T) dependent dielectric constants were measured using the alternating current (AC) impedance method with an ITO sandwich electrode. Since **C8Trip** sublimates at temperatures above 400 K, it was evaluated under reduced pressure in the T -range of 173–400 K (Figure 5) and under N₂ atmosphere in the T -range of 298–453 K (Figure S12). **C8[18]DBA** was evaluated in the T -range of 310–473 K under an N₂ atmosphere (Figure S13). The real part dielectric constant (ϵ_1) of **C8[18]DBA** was approximately 2.3 at 300 K, and a significant increase in ϵ_1 was observed around 430 K, where intermolecular polymerization reactions occur according to the TG chart. However, only a slight decrease of ϵ_1 was observed up to 420 K, and no f -dependence was observed. Therefore, **C8[18]DBA** does not exhibit molecular dynamics accompanied by changes in dipole moments in the crystalline phase (Figure S13).

In **C8Trip**, a f -dependent ϵ_2 peak was observed in the T -range of 252–343 K, and at the same time, a dielectric anomaly appeared in ϵ_1 response (Figure 5). An increase in ϵ_1 associated with the transition to a liquid near the melting point was confirmed (Figure S12). This corresponds to the presence of dielectric relaxation caused by molecular motion accompanied by changes in dipole moments within the molecular assembly. Fitting of the Debye-type relaxation process using the peak value of ϵ_2 yielded an Arrhenius-type linear relationship, yielding an activation energy (E_a) of 61.2 kJ mol⁻¹ and a prefactor of the relaxation time $\tau_0 = 4.08 \times 10^{-17}$ sec (Figure S14). The crystalline phase at $T = 272$ K exhibited a fast relaxation process with $\tau = 1.59 \times 10^{-4}$ sec, which is considered that motion attributable to β -relaxation similar to that of alkyl side chain rotational fluctuations in polymer materials occur. A similar relaxation process has also been observed in **C8[12]DBA** with $E_a = 52.3$ kJ mol⁻¹ and $\tau = 5.84 \times 10^{-16}$ sec (Figures S14, 15), indicating that both are governed by similar molecular motion.

C8[12]DBA shows a transition to a glassy state, whereas **C8Trip** forms a crystalline phase. The dielectric relaxation of both is thought to have common degrees of freedom due to flexible alkyl side chains. When these degrees of freedom are frozen, the weak intermolecular interactions of **C8Trip** form a crystalline phase, whereas **C8[12]DBA** forms a glassy state. **C8[12]DBA** can form effective π – π interactions between the [12]DBA cores. However, it is considered that structural relaxation without formation of π -dimers occurs upon freezing of the alkyl chain motion in the liquid state, leading to glass formation of **C8[12]DBA**. On the other hand, **C8[18]DBA** does not show clear dielectric relaxation, which is attributed to the hexagonal lattice of the π -stacking columns suppressing the molecular motion of the alkyl chains.

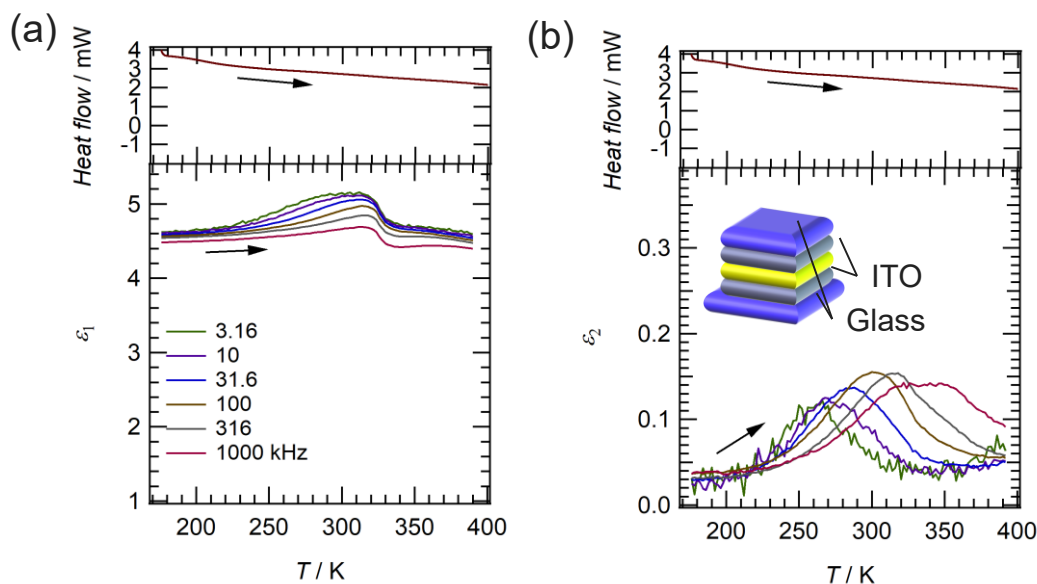


Figure 5. Temperature- and frequency-dependent (a) ϵ_1 and (b) ϵ_2 of **C8Trip** and DSC chart in the heating process under reduced pressure. Inset is schematic diagram of measurement sample cell.

3.7. Optical properties. To discuss the relationship between molecular assembly structure and optical properties, the absorption-fluorescence spectra and absolute quantum yields of **C8[18]DBA** and **C8Trip** were compared with those of **C8[12]DBA** (Figure 6, Figure S16, and Table S4). The absorption spectrum of **C8[12]DBA** in CHCl_3 showed a weak absorption at 370 nm and a strong

absorption maximum at 332 nm with molar absorption coefficient $\varepsilon = 2.17 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ (Figure S16). Additionally, the fluorescence spectrum in CHCl_3 exhibited a fluorescence maximum at 511 nm, with shoulders at 470, 523, and 560 nm, and a quantum yield of 13%. Due to the D_{3h} symmetric frontier orbitals of the **[12]DBA** π -core, the $S_0 \rightarrow S_1$ transition is forbidden (Figure S5), and the observable transition band is the $S_0 \rightarrow S_2$ transition at 332 nm. The small absorption band at 370 nm corresponds to the $S_0 \rightarrow S_1$ transition, which is a forbidden transition. On the other hand, the fluorescence process is contributed to by non-radiative process and phosphorescence resulting from the relaxation process via the $S_1 \rightarrow S_0$ transition and the relaxation process via charge transfer from the 12-membered annulene ring to the benzene ring. The large Stokes shift of $10,500 \text{ cm}^{-1}$ is a result of the previously mentioned optical process.

C8[18]DBA in CHCl_3 exhibited an absorption maximum at 356 nm with $\varepsilon = 1.02 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ and had vibrational structures at 258, 286, 304, 333, 380, and 391 nm. The absorption maximum corresponds to the $S_0 \rightarrow S_1$ transition, which differs from the results for **C8[12]DBA**. This is because the threefold symmetry of the frontier orbitals is broken, allowing HOMO–LUMO transition (Figure S6). The fluorescence spectrum exhibited vibrational structures at 416 and 441 nm, with a fluorescence maximum observed at 452 nm, yielding a quantum yield of 29% and a Stokes shift of $5,970 \text{ cm}^{-1}$. The observation of vibrational structures in the absorption-fluorescence spectra is consistent with the optical properties of the bare **[18]DBA**. On the other hand, the absorption spectrum of **C8Trip** in CHCl_3 shows a strong absorption maximum at 310 nm with $\varepsilon = 1.47 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, and the fluorescence spectrum shows a fluorescence maximum at 391 nm. The quantum yield and Stokes shift were 11% and $6,670 \text{ cm}^{-1}$, respectively. Since the $S_0 \rightarrow S_1$ transition is an allowed in **C8Trip**, it exhibited absorption-fluorescence behavior similar to that of **C8[18]DBA** (Figure S7).

The absorption-fluorescence spectra of solid-state **C8[18]DBA** and **C8Trip** were compared with those of glass-state **C8[12]DBA**. The glass state of **C8[12]DBA** exhibited an absorption maximum at 332 nm, and its spectral shape was consistent with that of the solution state (Figure 6a). The absence

of a significant red shift in the absorption maximum in the glass state indicates the absence of significant intermolecular interactions, corresponding to the D_{3h} symmetry of frontier orbitals for the **DBA** π -core. On the other hand, the optical properties of **C8Trip** and **C8[18]DBA**, which form crystalline phases, differed between the solution and solid phases. The fluorescence spectrum of **C8[18]DBA** in the solid state exhibited a fluorescence maximum at 471 nm, and the vibrational structure had disappeared, which was different from that in the solution state (Figure 6b). This is due to the presence of effective intermolecular interactions, similar to other **[18]DBA** derivatives. Additionally, the luminescence quantum yield of 2% of **C8[18]DBA** in the solid state was significantly reduced compared to the solution state, suggesting aggregation-induced quenching (ACQ) due to significant π - π interactions in the solid state. Similarly, the absorption maximum of **C8Trip** in the solid state (313 nm) exhibited only marginal red shift compared to the solution state (Figure 6c). The luminescence quantum yield of **C8Trip** in the solid state decreased from 11% in the solution state to 6%, exhibiting ACQ similar to that of **C8[18]DBA**. Since the frontier orbital coefficients of **C8Trip** extend to the phenylene units at the molecular ends, it is considered that red shift and ACQ of fluorescent spectrum in the solid state was exhibited due to intermolecular interactions between the phenylene units (Figure S7).

To gain insights into fluorescence quenching, we measured the fluorescence lifetime in CHCl_3 and in the solid state at 298 K (Figures S17, 18, and Tables S5, 6). The fluorescence decay curve of **C8[12]DBA** in CHCl_3 solution at a wavelength of 513 nm was well fitted with three components of life time constants: 7.55 ns, 17.1 ns, and 1.43 ns. When compared to the fluorescence lifetime measurements of **C1[12]DBA** in DMF solution at wavelength of 520 nm reported by Douhal et al., the 1.43 ns and 7.75 ns life time constants can be attributed to emission from two charge-transfer states S_1 , while the 17.1 ns time constant can be attributed to emission from the T_1 state. On the other hand, the fluorescence decay curve at wavelength of 523 nm in the glass state was reproduced with 6.36 and 27.7 ns, and the emission from the shortest-lived charge-transfer species S_1 had disappeared. This

phenomenon was also observed in fluorescence lifetime measurements of **C1[12]DBA** in the crystalline state and is the main cause of the red shift in the fluorescence spectrum. The fluorescence decay curve of **C8Trip** in CHCl_3 at a wavelength of 390 nm was well-fitted with a single component life time constant of 11.5 ns. On the other hand, the fluorescence decay curve of **C8Trip** in the solid state at a wavelength of 410 nm was fitted with two components of life time of 5.70 and 15.7 ns, suggesting the presence of excimer emission due to intermolecular interactions between phenylene units at the molecular ends. Compared to the solution state, in the solid state of **C8Trip**, the intermolecular interactions between phenylene units with frontier orbitals caused a red shift in the fluorescence spectrum and a decrease in the emission quantum yield. For **C8[18]DBA**, the fluorescence decay curve at wavelength of 455 nm in CHCl_3 was reproducible with life time constants of 1.03 and 2.18 ns. This decay process also yields similar results for the peaks observed at 410, 440, and 455 nm in the emission spectrum. On the other hand, the solid state **C8[18]DBA** exhibited a significant decrease in fluorescence lifetime, with the fluorescence decay curve at wavelength of 473 nm being reproducible with life time of 654 ps and 1.34 ns. This is a result of increased non-radiative decay process due to the formation of non-luminescent excimers, consistent with the significant decrease in fluorescence quantum yield observed in the solid state. The ACQ and the crystallinity of the molecular aggregate structure of **C8Trip** and **C8[18]DBA** governed the optical properties.

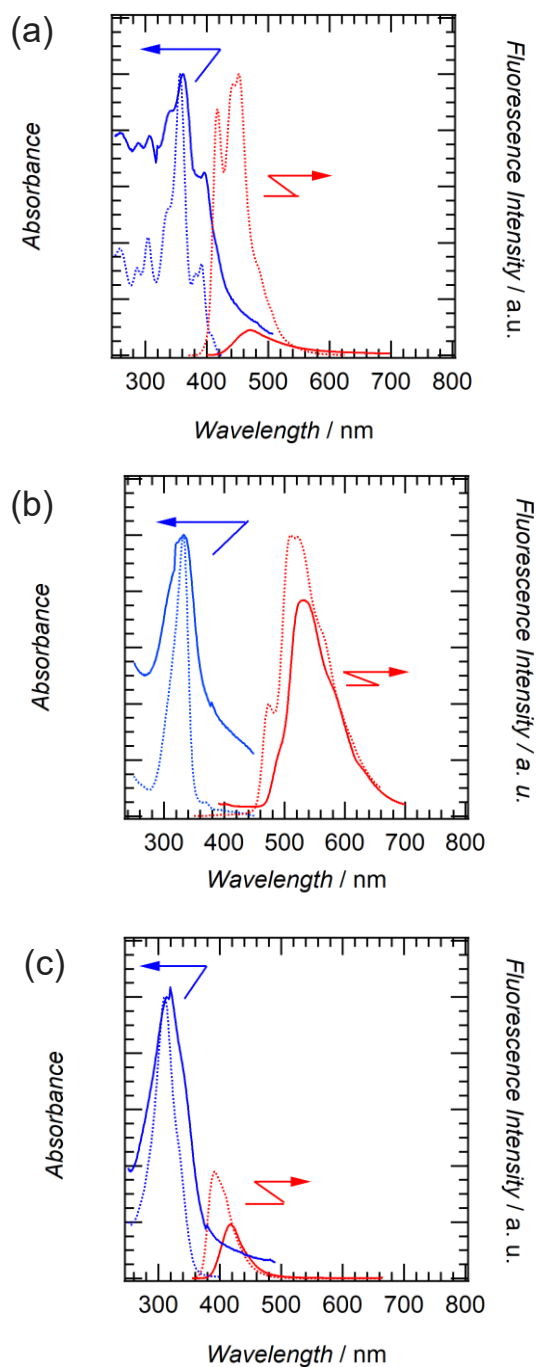


Figure 6. Absorption-fluorescence spectra in CHCl_3 and in the solid in KBr pellets. Blue and red spectra are absorption and fluorescence spectra, respectively. Solid and dash line spectra are solid and solution spectra, respectively. (a) **C8[12]DBA** for the excitation wavelengths for solution and solid are $\lambda_{\text{ex}} = 350$ and 340 nm, respectively. (b) **C8[18]DBA** for the excitation wavelengths for solution and solid are $\lambda_{\text{ex}} = 395$ and 395 nm, respectively. (c) **C8Trip** for the excitation wavelengths for solution

and solid are $\lambda_{\text{ex}} = 310$ and 310 nm, respectively. The vertical axis of the fluorescence spectra is normalized based on the quantum yield of **C8[18]DBA** in solution (29%).

4. Conclusion

We compared the molecular assembly structures, dielectric properties, and optical properties of **C8[18]DBA** and **C8Trip** with those of **C8[12]DBA**, a molecular glass with same C_3 -symmetry, the same terminal substituents and different central ring size. **C8[18]DBA** and **C8Trip** formed crystalline solid phases with heterogeneous 1D columnar structures composed of π -dimers. In particular, effective π - π interactions were observed in **C8[18]DBA**, forming a hexagonal lattice of 1D columns. Single-crystal X-ray structural analyses of methylbenzoate derivatives revealed that the π - π interactions and steric hindrance between terminal phenylene units varied depending on the ring size. Furthermore, dielectric constants showed that **C8[12]DBA** and **C8Trip** exhibited dielectric relaxation with similar activation energies derived from the thermal motion of alkyl ester chains, although glass and crystalline phases were due to differences in their freezing patterns upon cooling. On the other hand, **C8[18]DBA** exhibited no dielectric relaxation phenomenon due to the suppression of molecular motion by effective π - π interactions. The optical properties of each compound showed that **C8[12]DBA** exhibited similar spectra in both solution and solid states, while **C8[18]DBA** and **C8Trip** exhibited a significant decrease in luminescence intensity in the solid state, confirming ACQ. It was demonstrated that molecular assembly structures significantly influence optical properties, and successful guidelines for designing luminescent molecular glasses were established. In the future, by clarifying the correlation between the formation of molecular assembly structures and chemical structures using methods such as molecular dynamics simulations, it will be possible to design more sophisticated molecular glasses.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on KAKENHI (Grant Numbers: JP20H05865, JP23K13715, JP24H01727, JP24K01452, JP24K01468, JP24K01475), ACT-X (Grant Numbers: JPMJAX23DF), JST SPRING (Grant Number: JPMJSP2114), the establishment of university fellowships towards the creation of science technology innovation (Grant Number: JPMJFS2102), Izumi Science and Technology Foundation, and the “Crossover Alliance to Create the Future with People, Intelligence and Material” project supported by the Ministry of Education, Culture, Sports, Science, and Technology.

ASSOCIATED CONTENT

Supporting Information Available. Experimental section, electronic structures, TG curves, PXRD patterns of **C8[18]DBA** after polymerization, POM images of **C8[12]DBA**, molecular assembly structures of **C8[n]DBAs** and **C8Trip**, single crystal structures of **C1[n]DBAs** and **C1Trip**, PXRD patterns of **C8[n]DBAs** and **C8Trip**, dielectric constants of **C8[n]DBAs** and **C8Trip**, optical properties of **C8[n]DBAs** and **C8Trip**, fluorescence lifetime of **C8[n]DBAs** and **C8Trip**, NMR spectra, HRMS spectrum, and cartesian coordinates. This material is available free of charge at <http://pubs.acs.org>.

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