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Regioselectivity control of photodimerization of liquid-crystalline cinnamoyl compounds by phase variation: dual functionality of *p*-terphenyl substituent as a mesogen and a triplet sensitizer

Hideyuki Kihara^{a,*}, Yasuo Norikane^b, Masaru Yoshida^{a,*}

^a Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan ^b Electronics and Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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ABSTRACT

Cinnamoyl-functionalized liquid-crystalline (LC) compounds having a 4"-substituted [1,1';4',1"]terphenyl (*p*-terphenyl) as mesogens were synthesized to investigate the abilities of the mesogen to act as a triplet sensitizer. UV (365 nm) irradiation of the LC compound having 4"-cyano-*p*-terphenyl in the crystalline and LC phases regioselectively produced the photodimers with a head-to-tail and a head-to-head cyclobutane unit, respectively. The *p*-terphenyl thus played the role of triplet sensitizer because the cinnamoyl group does not absorb 365 nm light. Due to the dual functionality of the *p*-terphenyl as the mesogen and the triplet sensitizer, we successfully performed the photochemical and regioselective cycloaddition to obtain two different LC dimers from one LC monomer.

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1. Introduction

Photocycloaddition of a cinnamoyl group is one of the useful synthetic techniques for the dimerization and cross-linking of organic compounds in order to prepare a variety of functional materials, e.g., liquid crystal alignment films, holographic recording materials, crack healing materials, and nanogels for drug delivery.^{1–5} One of the most unique features of the reaction is the regio- and stereo-selectivity at the cyclobutane unit. It has been well understood that the molecular structure of a cyclobutane unit resulting from the [2+2] cycloaddition by direct photo-excitation of cinnamic acid in the crystalline phase is closely related to the crystal packing (topochemistry).^{6–9} Therefore, the crystal engineering approach to control the structure of the cyclobutane unit using the crystalline condition has already attracted much attention.¹⁰

Meanwhile, for the practical examples for photocycloaddition of a cinnamoyl group, indirect photo-excitation by using a triplet sensitizer in the non-crystalline condition has often been employed instead of the direct excitation.^{11–14} This is because UV light shorter than ca. 300 nm, which is necessary for the direct excitation of a cinnamoyl group, is likely to decompose certain parts of the starting

organic compounds. In addition, the efficiency of the photocycloaddition is significantly improved using triplet sensitizers.^{11–14} Actually, cinnamoyl groups attached to amorphous polymers or liquid-crystalline (LC) polymers as their side chain have been dimerized through indirect photo-excitation using a triplet sensitizer additive, in order to cross-link the polymers.^{15–17} In some cases, the triplet sensitizer was covalently connected to the polymer backbone and the photodimerization of the cinnamoyl group by intramolecular triplet energy transfer was carried out.^{18–20} However, to the best of our knowledge, the photodimerization of the cinnamoyl moiety via triplet energy transfer in a crystalline (or LC) phase has not yet been well examined.

As another important issue, the dimerization of LC compounds, that is, the connection of two LC monomers by a covalent bond is one of the powerful tools for the tuning of the LC properties.^{21–28} LC dimers have shown very different properties from the corresponding monomers. Fig. 1 shows typical examples of the LC dimer structures. In a *linear* dimer, two mesogens locate on the opposite side relative to a connection unit, while two mesogens exist on the same side relative to the connection unit in a *U*-shaped dimer. Among the LC dimers based on the same mesogens, their LC properties significantly vary when they have different regio- and/or stereo-chemical geometries.^{29,30} Therefore, the regioselectivity control of the LC dimer structure has been thoroughly required to precisely tune the LC properties.





^{*} Corresponding authors. Tel.: +81 29 861 4442 (H.K.); tel.: +81 29 861 9422 (M.Y.); e-mail addresses: h-kihara@aist.go.jp (H. Kihara), masaru.yoshida@aist.go.jp (M. Yoshida).



Fig. 1. Schematic structures of (a) linear and (b) U-shaped LC dimers.

In a previous study, we successfully obtained the LC dimers by UV irradiation of the LC monomers having a cinnamoyl group in their LC phases in the presence of Michler's ketone (MK: 4,4'-bis(N,Ndimethylamino)benzophenone) as a triplet sensitizer.^{31,32} The cyclobutane units resulting from the [2+2] photocycloaddition of the cinnamoyl group exclusively had a head-to-head (HH) configuration, while only a trace amount of head-to-tail (HT) isomers were observed. Consequently, the dimers adopted the U-shaped geometry in their LC phases. It should be noted that this regioselectivity does not come from the LC ordering fields. It was already reported that the photodimer with the HH cyclobutane unit was significantly obtained by UV irradiation of an ethyl cinnamate in the molten state because the reaction intermediates of the HH photodimer were thermodynamically more stable than that of the HT isomer.³³ If it is possible to conduct photocycloaddition of cinnamoyl-containing LC compounds via an intramolecular (or an intermolecular) triplet energy transfer in the crystalline phase, the cyclobutane configuration of the products will be governed by topochemistry rather than thermodynamics. In other words, we can expect to tune the HH or HT geometries of the LC dimer by phase variation between the crystalline and LC states, if the molecular structures in the crystalline state are suitable for the HT dimer formation.

Based on the synthetic strategy, we have designed new cinnamoyl-functionalized LC compounds, as shown in Fig. 2. The key to the molecular design is the 4"-substituted [1,1';4',1'']terphenyl (*p*-terphenyl). The *p*-terphenyl group is known as a mesogen, which allows high isotropization temperatures and a wide temperature range of LC phases.^{34,35} In addition, the *p*-terphenyl is also anticipated as a triplet sensitizer to excite the cinnamoyl group, because the existence of the relatively stable triplet-excited state of *p*-terphenyl has already been reported.³⁶ In the present study, polar substituents, such as cyano (1), nitro (2), and *N*,*N*-dimethylamino (3) groups, were introduced at the 4" position of the *p*-terphenyl substituent to increase not only the molar extinction coefficient at



Fig. 2. Chemical structures of cinnamoyl-functionalized LC monomers **1**, **2**, and **3** having *p*-terphenyl mesogens used in this study.

365 nm,^{37,38} but also the mesomorphic ability of the compounds.³⁹ We investigated the photodimerization of the LC monomers in their crystalline and LC phases by indirect photo-excitation of the dimerizable group via the *p*-terphenyl moiety and the properties of the obtained compounds in order to clarify the dual functionality of the *p*-terphenyl units as the mesogens and triplet sensitizers. We also evaluated the effect of the auxiliary triplet sensitizer additive on the photoreaction in the LC phase. In addition, the regiose-lectivity of the photodimerization based on the crystalline and LC phases and difference in the LC phases of the obtained photodimers associated with regio-isomerism are described.

2. Results and discussion

2.1. Syntheses and properties of the LC monomers

We used the Suzuki coupling reaction for the syntheses of the *p*-terphenyl mesogens. The cinnamate monomers **1** and **2** having cyano-*p*-terphenyl and nitro-*p*-terphenyl groups were prepared by a similar synthetic route, as shown in Scheme 1. Due to the low solubility of the synthetic intermediate compound, 4-(6-bromohexyloxy)-4"-*N*,*N*-dimethylamino-*p*-terphenyl, in common organic solvents, we performed the Suzuki reaction as the final step for the synthesis of **3**, as shown in Scheme 2. The details of the synthesis are described in the Experimental section.



Scheme 1. Synthetic route to cinnamoyl-functionalized *p*-terphenyl LC monomers 1 and 2.



Scheme 2. Synthetic route to LC monomer 3.

The three monomers **1**, **2**, and **3** have thermotropic LC phases. Their phase transition temperatures determined by both differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) are listed in Table 1. Schlieren textures were observed for the monomers **1** and **2** in their respective nematic temperature range. A texture, in which focal-conic fans and homeotropic regions simultaneously existed, was also seen in the smectic A phase of **1**. In contrast to **1** and **2**, **3** showed only an unidentified smectic phase

 Table 1

 Transition temperatures and enthalpy changes for the monomers 1, 2, and 3 during the first heating and the first cooling scans

Monomer	Phase transition temperature ^a (°C) (ΔH (kJ mol ⁻¹))
1	Cr 140 (36.5) N 183 (0.19) I I 180 (0.42) N 134 (—) ^b SmA 87 (2.90) SmX 77 (22.7) Cr
2	Cr 158 (39.5) N 172 (0.26) I I 169 (0.50) N 127 (36.1) Cr
3	Cr 145 (36.5) SmX 208 (18.5) I I 204 (18.1) SmX

^a Cr=crystalline phase; SmX=unidentified smectic phase; SmA=smectic A phase; N=nematic phase; I=isotropic phase.

^b Not seen by DSC.

(SmX) after melting at 145 °C and changed to the isotropic phase at 208 °C during the first heating. The SmX phase of **3** was found to be a highly-ordered smectic phase by POM and X-ray diffraction (XRD) measurements. Upon subsequent cooling and heating, **3** showed no crystallization, but SmX–I and I–SmX transitions. The crystalline phase of **3** was only obtained by recrystallization from the solution, while it did not form from the melt by cooling.

The UV-vis absorption spectra of the monomers 1, 2, and 3 are shown in Fig. 3. The absorption maxima and the molar extinction coefficient at 365 nm of the monomers are shown in Table 2. Since it has been reported that the 4-methoxy-p-terphenyl shows an absorption maximum at 285 nm (in cyclohexane),⁴⁰ the red shifts of the spectra observed in Fig. 3 were considered to be due to the substituent effect of the polar groups at the 4"-position of the terphenyl. For comparison, the structure and the absorption spectrum of 4-(4-(hexyloxy)benzoyloxy)phenyl 4-(6-(cinnamoyloxy)hexvloxy)benzoate (8), which was used for the photodimerization with MK in the previous study,³¹ are also shown in Fig. 3. While **8** had no absorption at 365 nm, 1, 2, and 3 with terphenyl chromophores showed certain absorptions in the long wavelength region. This result clearly showed that the terphenyl mesogens are origins of the longer absorptions and they can be selectively excited by 365-nm UV light. It is then expected that the mesogens would be able to sensitize the cinnamoyl group through a triplet energy transfer.



Fig. 3. UV–vis absorption spectra of **1**, **2**, **3**, and **8** (for comparison) in dichloromethane solutions (c=0.03 mM).

2.2. UV irradiation in the crystalline phases

2.2.1. Photoproduct analyses of **1**, **2**, and **3**. It has been reported that the aromatic nitro compounds behave as an inter- and intramolecular triplet sensitizer for the photodimerization of a cinnamate group attached to polymers as a side chain in the LC or

Table 2

Absorption maxima (λ_{max}) and molar extinction coefficient (ε), and ε at 365 nm of the monomers **1**, **2**, and **3** in dichloromethane

Monomer	$\lambda_{\max} (nm) (\epsilon (M^{-1} cm^{-1}))$	$\epsilon_{365 nm} (M^{-1} cm^{-1})$
1	300 (38,600)	500
2	270 (34,200), 346 (21,700)	17,800
3	281(44,400), 324 (50,800)	5830

amorphous phase.^{11,16–20} However, it has not been clarified if such an inter- and intramolecular triplet sensitization occurs in the low molecular weight cinnamoyl compounds in the crystalline phase. In order to investigate the sensitizing ability of the terphenyl mesogens in the present study, the monomers **1**, **2**, and **3** were irradiated with 365-nm UV light in the crystalline state. We prepared a number of thin-layer crystalline samples of **1** and **2** by cooling their melts to ensure reproducibility of the photoirradiation experiments. As for **3**, the powdery crystals prepared from an ethanol solution were used for the UV irradiation, because a crystalline sample was not obtained from its melt by cooling. Since the cinnamoyl group does not directly absorb the UV light as already described, observation of the cycloaddition reaction under this condition should mean that the terphenyl mesogens have the potential of being a triplet sensitizer in order to transfer the energy to the cinnamoyl moiety.

Gel permeation chromatography (GPC) charts measured after the UV irradiation of 1, 2, and 3 at room temperature for specific times are depicted in Fig. 4. As shown in the charts of 1 and 2, the peaks of the monomers at around 12.8 min decreased, while the peaks at shorter elution times than the monomers appeared after the UV irradiation, showing the progress of the photoreaction. We confirmed that the early-eluted new peaks corresponded to the photodimers not only by NMR but also by Matrix-Assisted Laser Desorption/Ionization Time-of-Flight MS (MALDI-TOF MS). The intensity of the dimer peak of 1 gradually increased with the increasing irradiation time, while the reaction rate was much slower than that of 2. However, the final conversions from the monomers to the corresponding dimers were almost identical in both cases. In contrast to 1 and 2, the UV irradiation of the crystal of 3 with a dimethylamino substituent as the electron-donating group produced only a slight amount of the corresponding dimer, although the monomer was certainly consumed during the photoirradiation. We eventually found that the insoluble portions in tetrahydrofuran (an eluent for GPC analysis) were mainly produced after the UV irradiation of **3**, indicating that an undesirable byproduct occurred during the UV irradiation of 3. Although the reason for the difference in the photoreactivity observed for 3 is still unclear, we eventually found that at least the two monomers 1 and 2 having the electron-withdrawing groups successfully gave the corresponding photodimer in the crystalline state.



Fig. 4. GPC charts of **1**, **2**, and **3** obtained by UV (365 nm) irradiation in the crystalline phases at room temperature for various periods of time.

In order to elucidate the regioselectivity of the cyclobutane units resulting from the UV irradiation of the crystals of **1** and **2**, their ¹H NMR measurements were performed. Fig. 5 shows the ¹H NMR spectra of the monomer of **1** and the sample irradiated by UV light



Fig. 5. ¹H NMR spectra of **1**: (a) before and (b) after UV (365 nm) irradiation in the crystalline phase for 2 h. Arrows indicate peaks of the cyclobutane units.

for 2 h in the crystalline phase. The olefinic proton peaks corresponding to the cinnamoyl group (two doublets at 6.45 and 7.69) decreased, while new peaks associated with the cyclobutane units (around 3.72, 3.96, and 4.46) appeared after the UV irradiation. Furthermore, it was confirmed by the 2D (¹H–¹H correlated spectroscopy) NMR spectrum (see Fig. S9 in Supplementary data) that the peaks at 3.96 and 4.46 ppm had a coupling and the multiplet peaks at around 3.72 ppm consisted of two sets of coupling peaks. Because no coalescence of these peaks was observed in high temperature ¹H NMR at 100 °C, we concluded that the peaks were originated from a mixture of two HT isomers. We thus assigned the peaks at 3.96 and 4.46 ppm to the α -type cyclobutane, and the peaks at around 3.72 ppm to the ε -type cyclobutane, based on the previous literatures.^{41–45} These parts including two phenyl rings were known to be truxillates and had HT configurations, as indicated in the inset of Fig. 5. This result is in clear contrast to the fact that the HH isomers were dominantly obtained upon UV irradiation of the cinnamoyl-functionalized LC monomers in their LC phases in our previous study.^{31,32} A similar result was also obtained for the ¹H NMR measurement of the UV-irradiated crystalline sample of 2, suggesting an HT configuration of the photodimer. We thus considered that the *p*-terphenyl groups behaved as a triplet sensitizer even in the crystalline state, ensuring the highly regioselective formation of the HT dimers.

2.2.2. Phosphorescence spectroscopy of the precursors of 1 and 2. To investigate the triplet energy of the *p*-terphenyl mesogens of **1** and 2, phosphorescence spectroscopy was carried out in a frozen glass under low temperature conditions. In this case, the corresponding precursors 5 and 6 were used for the phosphorescence experiments. (The structures of 5 and 6 are depicted in Scheme 1.) The main reason why the precursors were used instead of the monomers 1 and 2 was to take into account the possibility of phosphorescence quenching by an intramolecular energy transfer from the triplet-excited mesogens to the reactive cinnamoyl group during the measurements. Phosphorescence emissions were detected from both of the precursors 5 and 6 in methylcyclohexane matrices at 77 K (see Fig. S10 in Supplementary data). The triplet energies of **5** and **6** were estimated to be 245 and 232 kJ mol⁻¹, respectively, from the onsets of the corresponding phosphorescence bands based on Kasha's rule.⁴⁶ These values are sufficiently higher than that of the typical cinnamate compound, i.e., methyl cinnamate (229 kJ mol⁻¹).⁴⁷ Although the phosphorescence spectroscopy measurements of **1** and **2** in the crystalline state are not yet available, the present result obtained from the solution spectroscopy of the precursors should suggest that the *p*-terphenyl mesogens play a role as a triplet sensitizer.

2.2.3. Crystallographic analysis of the single crystal of 1. To clarify the topochemistry during the photodimerization in the crystalline state. X-ray crystallography was performed for the single crystal of the monomer **1**. The single crystal of **1** for this experiment was obtained by the recrystallization from a mixed solution of dichloromethane and hexane. The obtained structure is shown in Fig. 6. (CCDC-844056 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.) The cinnamoyl group exhibited a head-totail fashion to the adjacent one, and moreover, the olefinic double bonds are very close and almost overlapped parallel to each other with the distance between them of 4.06 Å. This intermolecular distance meets the necessary condition for solid-state photocycloaddition⁶⁻⁹ and totally coincident with the fact that the HT cyclobutanes were exclusively obtained by the UV irradiation of 1 in the crystalline phase. From the crystal structure, the *p*-terphenyls are in an anti-parallel configuration, probably due to the strong dipole-dipole interaction of the highly polarized mesogen induced by the cyano group. Therefore, the mesogen should eventually promote the self-assembled structure of the neighboring molecules that is preferable for the HT dimerization in comparison to the HH one. The crystal packing determined by the X-ray crystallography of the single crystal of **1** seemed to be suitable for the exclusive formation of α -truxillate, that is, svn-HT isomer by the photocvcloaddition. However the other *e*-truxillate, that is, *anti*-HT isomer was actually formed to give a mixture of HT dimers, as indicated by the NMR measurement. This is probably due to polymorphism in the thin-layer crystal samples used for the photodimerization or the local movement of the molecule during the photoreaction process. Note that the cyclobutane regio-isomers were occasionally obtained by the photochemical [2+2] cycloaddition of styryl compounds even in the crystalline phase,^{44,48} as similar to the present ones.

Compound **2** with a nitro group also exclusively gave the HT dimer as described. Although the suitable single crystals of **2** were



Fig. 6. Crystal structure of **1** obtained from X-ray crystallographic analysis: (a) unit cell viewed along *b*-axis and (b) one of the HT arranged (based on the cinnamoyl group) molecule pairs in the crystal.

not obtained in the present study, we assume that a similar geometry in the crystal induced by the dipole–dipole interaction should be possible for compound **2**, thus leading the regioselective dimerization reaction.

Based on these experimental results, we have concluded the following (Fig. 7). The UV (365 nm) irradiation of **1** or **2** in their crystalline states induced an excitation of the *p*-terphenyl mesogens and then the excited mesogens sensitized the cinnamovl group through an intramolecular (or intermolecular) triplet energy transfer in the crystals. The triplet-excited cinnamoyl moieties underwent the intermolecular cycloaddition reaction with the neighboring one. Since the photodimerization regioselectively took place, the resulting cyclobutane units exclusively had the HT configuration based on the initial crystal packing. As we already described, there has been a number of reports on the aromatic nitro compounds as a triplet sensitizer for the photodimerization of a cinnamate group in amorphous and LC polymers.^{11,16–20} To the best of our knowledge, the present study is the first example, which reveals that aromatic nitro and cyano compounds serve as triplet sensitizers for the cinnamoyl group even in the highly-ordered crystalline phases.



Fig. 7. Reaction mechanism for the formation of the HT dimers derived from **1** or **2** through triplet energy transfer from the photo-excited mesogens in the crystalline phases.

We also confirmed that the photodimers derived from **1** and **2** showed thermotropic LC phases based on both the POM and DSC measurements. It should be thus emphasized that the *p*-terphenyls still behave as mesogens to stabilize the LC state even after the photochemical formation of the bulky moiety in the molecular structure, that is, the four-membered truxillate resulting from the photocycloaddition of the cinnamoyl group. The detailed nature of the LC phases of the photodimers derived from **1** and **2** will be discussed in a later section.

2.3. UV irradiation in the LC phases

As mentioned above, the HT photodimers were selectively obtained by the UV irradiation of monomers **1** and **2** in the crystalline phases. In contrast, our previous studies revealed that HH photodimers were mainly formed by UV irradiation in their LC phases with MK.^{31,32} To discuss the difference in the regioselectivity depending on the phase variation, monomers **1**, **2**, and **3** were irradiated with UV light (365 nm) in their LC phases (at 170 °C for **1**, at 165 °C for **2**, and at 190 °C for **3**). The formation of the corresponding dimers was investigated by GPC measurements. The results are shown in Fig. 8. As a result, while the dimers of **1** and **2** actually appeared after the UV irradiation, a small amount of undesirable products with relatively high-molecular weights were also generated in both cases, and shown to be the broad shoulders of the peaks of the dimers. The formation of a byproduct was also



Fig. 8. GPC charts of the UV (365 nm) irradiated samples of **1**, **2**, and **3** in the LC phases at 170, 165, and 190 $^{\circ}$ C, respectively, for various times.

observed upon the UV irradiation of **3**, similar to the crystalline phase described in the previous section.

The ¹H NMR spectrum of **1** irradiated by the UV light at 170 °C for 30 min is depicted in Fig. 9. The peaks at 3.47 and 3.76 ppm showed coupling, corresponding to a δ -type cyclobutane as the HH isomer (truxinate, the structure was depicted in the inset of Fig. 9). The ¹H NMR spectrum of the UV-irradiated sample of **2** also revealed a similar NMR pattern to **1**, indicating the formation of the HH dimer. These results for the HH regioselectivity are the same as those from our previous study on the photodimerization of the cinnamoyl-functionalized LC monomers with MK.^{31,32}



Fig. 9. ¹H NMR spectra of the UV (365 nm) irradiated sample of **1** in the LC phase at 170 °C for 30 min. Arrows indicate peaks of the cyclobutane unit.

We also carried out the photoirradiation of the present monomers in their LC phases with MK as an auxiliary additive (2 wt %) to examine the effect of MK with the highly efficient triplet energy transfer ability on the photoreaction. The GPC charts of the photoirradiation experiments for 1 and 2 in the presence of MK are depicted in Fig. 10. As expected, the photodimer of 1 was efficiently and selectively obtained, resulting in the significant suppression of the generation of any undesirable byproduct. In contrast, the photodimerization of 2 under MK conditions proceeded with a low efficiency and the formation of an undesirable byproduct rather increased when compared to the condition without MK. Although the reason for the negative effect of MK for **2** is unclear, it can be considered that the generation of the byproduct from the photoreaction of **2** in the LC phase at high temperature should mainly be caused by the nitro group on the terphenyl part, which may induce hydrogen abstraction under the specific photochemical conditions as already reported.49



Fig. 10. GPC charts of the UV (365 nm) irradiated samples of **1** and **2** using MK in the LC phases at 170 and 165 $^{\circ}$ C, respectively, for various times.

Although UV–vis absorption spectra of 1, 2, and 8 in the solution state are already shown in Fig. 3, we also measured absorption spectra of the compounds in the condensed (crystalline and LC) phases in order to demonstrate that the triplet energy transfer takes place in those phases. As shown in Fig. S11 in Supplementary data, all the condensed-phase samples of 1 and 2 had the absorption band including the wavelength of 365 nm, whereas 8 did not show any absorption band at 365 nm. These results suggest that the absorption at 365 nm of **1** and **2** originates from the terphenyl groups but not from the cinnamoyl group even in the condensed phases. MK, which is widely-recognized as a triplet sensitizer, caused the dimerization of the cinnamovl-functionalized LC compounds under the condition of 365-nm irradiation in the condensed phase, and the same results were obtained when both 1 and 2 were irradiated with 365-nm light in the condensed phases without MK. Therefore, it is likely that the triplet energy transfer from the photo-excited mesogens to the cinnamoyl group of 1 and **2** took place in both the crystalline and LC phases.

We confirmed that the HH photodimer was regioselectively obtained by the UV (365 nm) irradiation of **1** in the LC phase with or without MK. This HH regioselectivity is in sharp contrast to that of the photodimerization in the crystalline phase. The reason for the drastic change in the regioselectivity is considered that the photodimerization in the crystalline phase was based on topochemistry whereas that in the LC phase was governed by thermodynamics.

2.4. LC properties of the photodimers of 1 and 2

From a comparison between the LC monomers and dimers, we observed that the photodimerization significantly changes the LC properties of the initial monomers. As for monomer 2, the photodimer was obtained only in the crystalline phase, and it adopted the HT configuration for the cyclobutane unit (*linear* dimer) as drawn in Fig. 1(a). The HT dimer of 2 (irradiation time: 12 h) exhibited a nematic phase from 201 to 190 °C and then a smectic A phase to 180 °C upon cooling. The isotropic-nematic phase transition temperature significantly increased compared to the monomer 2 by 32 °C. Note that the increase of the phase transition temperature is quite reasonable for the *linear* dimer formation.²¹ As already described, both of the photodimers having HT and HH cyclobutane units were selectively obtained in high conversion by the UV irradiation of **1**. Therefore, we examined the LC properties of the HT and HH dimers of **1**. As already described, the UV irradiation of **1** in the crystalline phase for 12 h selectively gave the HT dimer with the *linear* dimer structure, while the similar UV irradiation of **1** but in the LC phase with MK for 30 min exclusively provided the HH dimer with the Ushaped geometry as illustrated in Fig. 1(b). The phase transition temperatures of the dimers determined by DSC and POM are listed in Table 3. Focal-conic fans and homeotropic regions could be simultaneously observed in LC phases that appeared below the nematic phases of both dimers, therefore, the LC phases were identified as smectic A.⁵⁰ While the isotropization temperatures (T_i) of both dimers were higher than that of monomer **1**, the degree of T_i increase was greater for the HT dimer than that for the HH dimer. In contrast, the temperature range of the smectic A phase of the HH dimer was higher and wider than that of the HT dimer. It was already reported that when the *linear* and *U*-shaped LC dimers were compared based on the same mesogens, the former often shows a more thermally stable LC phase than the latter, whereas the latter tends to exhibit smectic phases compared to the former.^{29,30} Therefore, our present results are similar to previous observations.

Table 3

Transition temperatures and enthalpy changes for the HT and HH photodimers derived from **1** during the first cooling and the second heating scans

Photodimer	Phase transition temperature ^a (°C) (ΔH (kJ mol ⁻¹))
HT	Cr 183 (36.1) N 208 (1.89) I
	I 206 (1.93) N 183 (0.13) SmA 142 (33.2) Cr
HH	Cr 138 (10.5) 187 SmA (1.68) N 198 (1.60) I
	I 196 (1.85) N 185 (1.85) SmA 135 (10.1) Cr

^a Cr=crystalline phase; SmA=smectic A phase; N=nematic phase; I=isotropic phase.

To examine the geometric differences among the monomer, HH and HT dimers, XRD measurements were performed for 1 and both dimers in their smectic A phases. All the obtained XRD profiles were found to consist of one sharp peak in a small angle region corresponding to the smectic layer distance and a broad halo in the wide angle region associated with the lateral packing of the mesogens. Table 4 shows smectic layer distances (d) estimated from the sharp peaks in the XRD profiles and the molecular lengths of the all-trans conformation of the compounds (L) determined by molecular modeling based on molecular mechanics. First, as for monomer 1, d was longer than L, which indicated that in the smectic layer, the two molecules became paired with their cyano-pterphenyl mesogens interdigitated with each other. It was also suggested that the distance of the spatial overlapping of the molecules was almost the same as the length of the mesogen (about 1.5 nm), as shown in Fig. 11(a). It is well known that LC compounds having a cyanobiphenyl or cyano-*p*-terphenyl mesogen often show the LC structure with pairing of the mesogens in an anti-parallel manner due to the strong dipole-dipole interaction.⁵¹⁻⁵³ Next, as shown in Table 4, even after the photodimerization, the *d* value of the HH dimer was similar to that of 1. This result indicates that the HH dimer adopted the U-shaped conformation (L was estimated to be 3.08 nm by molecular modeling) and had an interdigitated structure in the smectic A phase, as shown in Fig. 11(b). Interestingly, the *d* of the HT dimer was found to be eventually smaller than that of **1** in contrast to the HH dimer. This result can be explained as follows. The HT dimer adopted the linear conformation (L was estimated to be 5.25 nm) in the smectic A phase. Therefore, the HT dimer had an intercalated structure with the two mesogens that overlapped at each molecular end, as shown in Fig. 11(c). The intercalation would be the main reason for the

Table 4

Smectic layer distances (d) and molecular lengths (L) for the monomer **1**, and the HT and HH photodimers

Compound	d ^a (nm)	L ^b (nm)
1	4.65	3.13
HH dimer	4.53	3.08
HT dimer	3.95	5.25

^a Determined by XRD in the smectic A phase.

^b Estimated by molecular modeling of fully extended chains.



Fig. 11. Schematic representation for self-assembled structures of the smectic A phases of (a) 1, (b) HH dimer, and (c) HT dimer derived from 1, estimated from XRD and molecular modeling.

decreasing *d* value. It is thus noteworthy that we successfully obtained both the *linear* and *U*-shaped LC dimers from the same LC monomer by a regioselective photoreaction based on the precise control of the reaction conditions.

3. Conclusions

In this study, three cinnamoyl-functionalized 4"-substituted-pterphenyl LC compounds were synthesized and their photochemical properties were carefully examined under several different reaction conditions. As a result, it was successfully found that the regioselective photodimerization of the LC compounds using the 4"-substituted p-terphenyls as unprecedented dual functional groups for the mesogens and the triplet sensitizers. Among the cyano- (1), nitro- (2), and N,N-dimethylamino- (3) substituted LC compounds, only 1 and 2 with electron-withdrawing groups underwent photodimerization with the appropriate reaction conditions. The photodimers with an HT cyclobutane configuration were regioselectively obtained in high yield from 1 and 2 by UV light (365 nm) irradiation in the crystalline phases, revealing that the pterphenyl moiety acted as a triplet sensitizer. Phosphorescence spectroscopy of the precursors of 1 and 2 suggested that the triplet state energies of the cyano- and nitro-substituted p-terphenyls are high enough to transfer energy to the cinnamoyl moiety. X-ray crystallography of the single crystal of 1 showed that the crystal packing between the double bonds was suitable for the solid-state photocycloaddition of the cinnamoyl group, supporting the HT dimer formation. In contrast, a photodimer with an HH cyclobutane unit was exclusively produced by the UV irradiation of **1** in the LC phase with or without Michler's ketone (MK) as the auxiliary triplet sensitizer, based on the thermodynamic stability of the intermediate of the HH dimer in the molten state at high temperature. The HT and HH photodimers from 1 and 2 showed thermally stable nematic and a smectic A phases, despite the existence of the bulky cyclobutane unit. Especially in case of 1, the XRD analyses of the photodimers in their smectic A phases proved that the HH and HT dimers adopted the interdigitated and intercalated structures, respectively. We consider that the present results for the

regioselective photodimerization of LC cinnamoyl compounds should be a productive method to selectively obtain the *linear* and *U*-shaped LC dimers from a variety of LC monomers. A related study on the tuning of the LC properties by this method is now in progress.

4. Experimental section

4.1. General methods

The ¹H, ¹³C, and 2D (¹H–¹H correlated spectroscopy) NMR spectra were recorded by a Varian Gemini 300BB (300 MHz) or a JEOL JNM-ECX400 (400 MHz) using TMS as the internal standard. Temperature dependent ¹H NMR was performed using the JEOL JNM-ECX400 and the experimental temperature range was from 25 to 100 °C (solvent: toluene- d_8). The UV-vis absorption spectra in the solutions were obtained using a Jasco V-570 spectrometer. The UV-vis absorption spectra of the thin-layer crystalline and LC samples of 1, 2, and 8 were measured by an Otsuka electronics MCPD-7000 using a transmittance mode. The samples were prepared between two cover glasses. The measurements of the crystalline samples were performed at room temperature. The temperatures of the LC samples (170 °C for 1, 165 °C for **2**, 150 °C for **8**) were controlled by a Linkam LK-600PH during the measurements. The phosphorescence spectra were recorded by a Jasco FP-777 spectrofluorometer using a PMA-281 unit to delay detection of the emission light. Solutions for the phosphorescence spectroscopy were deoxygenated by bubbling with nitrogen for 5 min prior to the measurements. IR spectra were recorded on a Jasco FT/IR-680 Plus. Gel permeation chromatography (GPC) was conducted using a Shimadzu system (an LC-10ADvp pump unit, an SPD-10Avp UV detector (detection wavelength: 320 nm for 1, 350 nm for 2, 330 nm for 3), a CTO-10Avp column oven, and an SCL-10Avp controller) with Shodex KF800D and KF805L columns, using THF as the eluent. The thermal properties of the samples were evaluated by polarized optical microscopy (POM) using an Olympus BH2 equipped with a Mettler FP82HT hot stage and by differential scanning calorimetry (DSC) using a Seiko Instruments, Inc., DSC 6200. The heating and cooling rates were $5 \,^{\circ}C \,^{-1}$. The powder X-ray diffraction patterns of the molten samples were measured at the LC temperatures using a Rigaku diffractometer (type 4037) with an imaging plate (R-Axis IV) or a Rigaku Rint2000. The single crystal X-ray diffraction measurement was performed at 183 K using a Bruker CCD area-detector diffractometer (Smart APEXII) with Mo-K α radiation. The single crystal of **1** suitable for the Xray diffraction measurements was obtained from the mixed solution of dichloromethane and hexane. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was conducted using an Applied Biosystems Voyager-DE Pro instrument operated in the reflector mode with 2,5dihydroxybenzoic acid as the matrix. Molecular modelings were performed using a Chem3D Ultra 8.0. The MM2 calculation and the geometry were fully optimized.

4.2. Synthesis

4.2.1. 4-Bromo-4'-(6-bromohexyloxy)biphenyl (4). A mixture of 4bromo-4'-hydroxybiphenyl (3.0 g, 12 mmol), 1,6-dibromohexane (15 g, 60 mmol), K₂CO₃ (2.5 g), and acetone (50 ml) was refluxed with stirring for 6 h. After cooling, the mixture was filtered, and the filtrate was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate=10:1 gradient to 5:1) and recrystallization from hexane to give **4** (3.7 g, 75%) as white crystals. Mp 192 °C. IR v_{max} (neat, cm⁻¹): 2939, 2863, 1604, 1473, 1245, 995, 809. ¹H NMR (300 MHz, CDCl₃) δ, ppm: 7.52 (d, *J*=8.6 Hz, 2ArH; H-4), 7.47 (d, *J*=8.8 Hz, 2ArH; H-2), 7.40 (d, J=8.6 Hz, 2ArH; H-3), 6.95 (d, J=8.8 Hz, 2ArH; H-1), 4.00 (t, J=6.4 Hz, 2H; OCH₂), 3.43 (t, J=6.8 Hz, 2H; BrCH₂), 1.93-1.80 (m, 4H; BrCH₂CH₂CH₂CH₂CH₂CH₂O), 1.55–1.50 (m, 4H; BrCH₂CH₂CH₂CH₂CH₂CH₂O). ¹³C NMR (100 MHz, CDCl₃) δ , ppm: 158.82, 139.69, 132.28, 131.72, 128.21, 127.90, 120.68, 114.82, 67.78, 33.80, 32.66, 29.07, 27.90, 25.29. MS (MALDI-TOF) C₁₈H₂₀Br₂O [M+H]⁺: 411.0; found: 410.2.

4.2.2. 4-(6-Bromohexyloxy)-4"-cyano-p-terphenyl (5). To a mixture of 4 (1.6 g, 4.0 mmol), Pd(PPh₃)₄ (0.46 g, 0.40 mmol), a 10% aqueous solution of Na₂CO₃ (10 ml), and THF (10 ml) was added THF (10 ml) containing the 4-cyano-phenyl-boronic acid pinacol ester (1.0 g, 4.4 mmol). The mixture was refluxed with stirring for 18 h. After cooling, the mixture was poured into water, and extracted three times with CHCl₃ (50 ml). The combined CHCl₃ was dried over MgSO₄, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/CHCl₃=1:1) and recrystallization from a mixture of toluene and ethanol to afford **5** (1.1 g, 56%) as white crystals. Mp 136 $^{\circ}$ C (nematic 236 °C isotropic). IR ν_{max} (neat, cm⁻¹): 2939, 2864, 2234, 1738, 1602, 1473, 1244, 995, 812. ¹H NMR (300 MHz, CDCl₃) δ, ppm: 7.73 (s, 4ArH; H-3,4). 7.68 (d, J=9.0 Hz, 2ArH; H-5 or 6), 7.64 (d, J=9.0 Hz, 2ArH; H-5 or 6), 7.57 (d, J=8.7 Hz, 2ArH; H-2), 6.99 (d, J=8.7 Hz, 2ArH; H-1), 4.02 (t, J=6.4 Hz, 2H; OCH₂), 3.44 (t, J=6.8 Hz, 2H; BrCH₂), 1.94–1.81 (m, 4H; BrCH₂CH₂CH₂CH₂CH₂CH₂CH₂O), 1.56-1.51 (m, 4H, BrCH₂CH₂CH₂CH₂CH₂CH₂CH₂O). ¹³C NMR (100 MHz, CDCl₃) δ, ppm: 158.95, 145.17, 141.15, 137.20, 132.59, 132.45, 128.04, 127.51, 127.44, 127.24, 118.96, 114.87, 110.72, 67.82, 33.81, 32.67, 29.09, 27.92, 25.31. MS (MALDI-TOF) C₂₅H₂₄BrNO [M+H]⁺: 433.5; found: 434.1.

4.2.3. 4-(6-Cinnamoyloxyhexyloxy)-4"-cyano-p-terphenyl (1). E-Cinnamic acid (94 mg, 0.63 mmol) and DBU (0.10 g, 0.67 mmol) were dissolved in dry dimethyl sulfoxide (DMSO; 15 ml). After stirring at 50 °C for 30 min, **5** (0.22 g, 0.51 mmol) was added and the mixture was left to stir for 3 h at 50 °C. After cooling, the mixture was poured into water (150 ml) and extracted three times

with CHCl₃ (50 ml). The combined CHCl₃ was dried over MgSO₄, filtered, and evaporated under reduced pressure. The residue was purified by recrystallization from $CHCl_3$ to give **1** (0.14 g, 56%) as white crystals. IR *v*_{max} (neat, cm⁻¹): 2945, 2869, 2225, 1698, 1636, 1598, 1489, 1469, 1175, 979, 811, 773. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 7.73 (s, 4ArH; H-3,4), 7.69 (d, J=16.1 Hz, 1 olefinic H; H-d), 7.67 (d, J=9.1 Hz, 2ArH; H-5 or 6), 7.64 (d, J=9.1 Hz, 2ArH; H-5 or 6), 7.56 (d, J=8.8 Hz, 2ArH; H-2), 7.53-7.51 (m, 2ArH; H-c), 7.39-7.37 (m, 3ArH; H-a,b), 6.99 (d, J=8.8 Hz, 2ArH; H-1), 6.45 (d, J=16.1 Hz, 1 olefinic H; H-e), 4.24 (t, *I*=6.6 Hz, 2H; COOCH₂), 4.04 (t, *I*=6.4 Hz, 2H; ArOCH₂), 1.88–1.74 (m, 4H; COOCH₂CH₂CH₂CH₂CH₂CH₂CH₂O), 1.56–1.51 (m, 4H, COOCH₂CH₂CH₂CH₂CH₂CH₂O). ¹³C NMR (100 MHz, CDCl₃) δ, ppm: 167.17, 159.12, 145.32, 144.75, 141.31, 137.31, 134.53, 132.72, 132.55, 130.33, 128.97, 128.16, 127.64, 127.57, 127.37, 119.08, 118.31, 115.02, 110.86, 68.02, 64.64, 29.28, 28.81, 25.92. MS (MALDI-TOF) C₃₄H₃₁NO₃ [M+H]⁺: 502.2; found: 501.7. Anal. Calcd for C₃₄H₃₁NO₃: C; 81.41, H; 6.23, N; 2.79%. Found: C; 81.43, H; 6.17, N; 2.71%.

4.2.5. 4-(6-Cinnamoyloxyhexyloxy)-4"-nitro-p-terphenyl (2). From the reaction of *E*-cinnamic acid (0.25 g, 1.7 mmol) and **6** (0.70 g, 1.5 mmol), 2 was obtained as yellow crystals by the same procedure used for **1**. Yield 0.57 g (71%). IR v_{max} (neat, cm⁻¹): 2950, 2868, 1698, 1634, 1594, 1513, 1473, 1339, 1176, 977, 815, 755. ¹H NMR (300 MHz, CDCl₃) δ, ppm: 8.31 (d, *J*=8.8 Hz, 2ArH; H-6), 7.78 (d, *J*=8.8 Hz, 2ArH; H-5), 7.69 (d, J=16.0 Hz, 1 olefinic H; H-d), 7.68 (s, 4ArH; H-3,4), 7.57 (d, J=8.7 Hz, 2ArH; H-2), 7.55-7.51 (m, 2ArH; H-c), 7.39-7.37 (m, 3ArH; H-a,b), 7.00 (d, J=8.7 Hz, 2ArH; H-1), 6.45 (d, J=16.0 Hz, 1 olefinic H; H-e), 4.24 (t, *J*=6.6 Hz, 2H; COOCH₂), 4.03 (t, *J*=6.4 Hz, 2H; ArOCH₂), 1.88-1.75 (m, 4H; COOCH₂CH₂CH₂CH₂CH₂CH₂O), 1.56-1.51 (m, 4H; COOCH₂CH₂CH₂CH₂CH₂CH₂O). ¹³C NMR (100 MHz, CDCl₃) δ , ppm: 167.16, 159.18, 147.27, 147.07, 144.75, 141.57, 136.88, 134.53, 132.46, 130.34, 128.97, 128.18, 128.15, 127.81, 127.59, 127.39, 124.26, 118.31, 115.04, 68.03, 64.64, 29.28, 28.81, 25.92. MS (MALDI-TOF) $C_{34}H_{31}NO_3 [M+H]^+$: 522.2; found: 521.7. Anal. Calcd for $C_{34}H_{31}NO_3$: C; 75.99, H; 5.99, N; 2.69%. Found: C; 75.79, H; 5.91, N; 2.60%.

 64.51, 29.14, 28.67, 25.78. MS (MALDI-TOF) C₂₇H₂₇BrO₃ [M+Na]⁺: 501.1; found: 501.4.

4.2.7. 4-(6-Cinnamoyloxyhexyloxy)-4"-N,N-dimethyamino-p-ter*phenvl* (**3**). 4-*N*.*N*-Dimethylamino-phenyl-boronic acid (0.30 g. 1.8 mmol), 7 (0.80 g, 1.7 mmol), and Pd(PPh₃)₄ (64 mg, 0.055 mmol) were dissolved in a mixture of dimethoxyethane (DME: 30 ml) and EtOH (15 ml). A 10 wt % ag Na₂CO₃ (10 ml) solution was added and the mixture was refluxed with stirring for 10 h. After cooling, the mixture was poured into water (100 ml) and the precipitate was collected by filtration. The crude product was purified by silica gel column chromatography (eluent: CH₂Cl₂) and recrystallization from EtOH to afford **3** (0.44 g, 51%) as pale yellow crystals. IR ν_{max} (neat, cm⁻¹): 2939, 2865, 2796, 1706, 1636, 1606, 1541, 1494, 1470, 1177, 807, 767. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3) \delta$, ppm: 7.69 (d, J=16.0 Hz, 1 olefinic H; H-d). 7.62 (d, *I*=8.8 Hz, 2ArH; H-3 or 4), 7.58 (d, *I*=8.8 Hz, 2ArH; H-3 or 4), 7.54–7.51 (m, 2ArH; H-c), 7.54 (d, J=8.8 Hz, 4ArH; H-2 and 5), 7.39-7.37 (m, 3ArH; H-a,b), 6.97 (d, J=8.8 Hz, 2H; H-1), 6.82 (d, J=8.8 Hz, 2H; H-6), 6.45 (d, J=16.0 Hz, 1 olefinic H; H-e), 4.23 (t, J=6.6 Hz, 2H; COOCH₂), 4.02 (t, J=6.4 Hz, 2H; ArOCH₂), 3.00 (s, 6H; N(CH₃)₂), 1.87-1.74 (m, 4H; COOCH₂CH₂CH₂CH₂CH₂CH₂O), 1.55-1.50 (m, 4H; COOCH₂CH₂CH₂CH₂CH₂CH₂CO). ¹³C NMR (100 MHz, CDCl₃) δ , ppm: 167.08, 158.51, 149.95, 144.63, 139.49, 138.43, 134.44, 133.34, 130.22, 128.87, 128.76, 128.06, 127.88, 127.54, 126.90, 126.50, 118.23, 114.78, 112.80, 67.88, 64.57, 40.61, 29.22, 28.72, 25.84. MS (MALDI-TOF) C₃₅H₃₇NO₃ [M+H]⁺: 520.3; found: 519.9. Anal. Calcd for C₃₅H₃₇NO₃: C; 80.89, H; 7.18, N; 2.70%. Found: C; 80.96, H; 7.17, N; 2.60%.

4.3. Photoirradiation in the crystalline phases

As for **1** and **2**, 2 mg of the monomer was placed between cover glasses (Matsunami Glass Ind., Ltd., Japan) and heated to the isotropization temperature using the Linkam hot stage. The molten sample was then cooled to room temperature at the rate of $5 \,^{\circ}$ C min⁻¹ and a thin-layer crystalline sample was obtained. The resulting sample was irradiated by monochromatic 365-nm UV light (5 mW cm⁻²) from a 500-W high-pressure mercury lamp through optical filters at room temperature. After completion of the UV irradiated sample was analyzed by several techniques. As for the monomer **3**, the powdery sample obtained by recrystallization from the EtOH solution was used for the UV irradiation in the crystalline phase. The sample (2 mg) between two cover glasses was spread as flat as possible and irradiated with UV light using the same procedure for **1** and **2**, except for not melting.

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Supplementary data

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