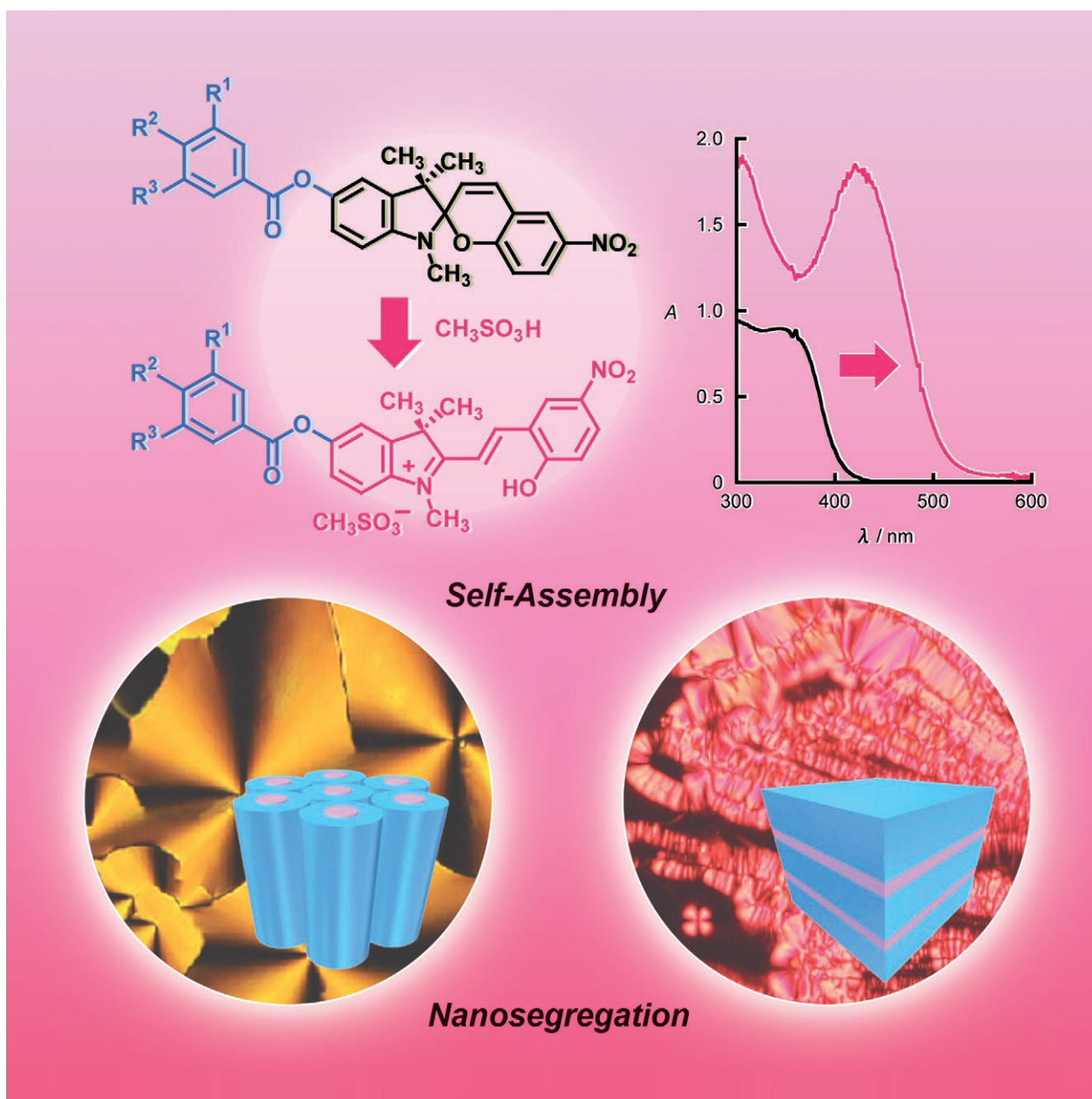# FULL PAPERS

Induction of Columnar and Smectic Phases for Spiropyran Derivatives: Effects of Acidichromism and Photochromism

Boon-Hooi Tan, Masafumi Yoshio, and Takashi Kato*[a]

Abstract: Liquid-crystalline (LC) properties have been induced in a number of spiropyran derivatives by the addition of methanesulfonic acid. Spiropyran derivatives containing one or two gallic acid moieties with one, two, or three long alkyl chains were prepared. Acid-induced spiro–protonated-merocyanine isomerization induced mesomorphism for these materials. Equimolar mixtures of methanesulfonic acid and the spiropyran derivatives with one or two dodecyloxy chains exhibited smectic A phases, whereas the spiropyran derivatives containing the gallic acid moiety with three dodecyloxy chains showed hexagonal columnar phases. On the contrary, photoirradiation of the spiropyran compounds in the bulk liquid state did not lead to the induction of mesomorphism, although the merocyanine form was induced. These results suggest that these merocyanine derivatives with ionic and nonionic moieties cannot simply form nanosegregated LC structures. Complex formation of the merocyanine form with methanesulfonic acid may play a key role in the formation of LC molecular assemblies.

Introduction

Liquid crystals are soft materials that form fluidic and ordered states of molecules.[1] A variety of functional nanostructures of liquid crystals has been reported.[2] Liquid-crystalline (LC) assemblies that can change their LC structures and molecular orientation in response to stimuli such as photoirradiation have attracted attention because stimuli-responsive liquid crystals have great potential as ordered materials exhibiting anisotropic and dynamic function. Photochromic compounds such as azobenzene[3] and spiropyran[4] have been used as dopants and mesogenic molecules. Gin and co-workers also reported acid-induced lyotropic mesomorphism for a chiral imidazolidinone derivative.[5]

Spiropyrans are unique compounds that show acid- and photochromic properties due to spiro–merocyanine isomerization.[6,7] This molecular transformation from the nonplanar and nonionic spiro (Sp) form to the planar and ionic merocyanine (MC) form is expected to promote the aggregation and formation of ordered nanostructures. Recently, we reported the induction of thermotropic columnar LC phases for a fan-shaped spiropyran derivative **1** (Scheme 1) by using 4-methylbenzenesulfonic acid as a stimulus.[8] Although **1** alone is nonmesomorphic, mixtures of **1** and the
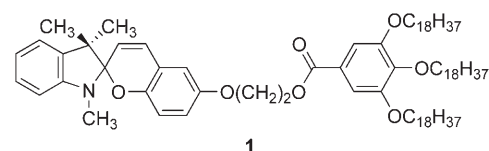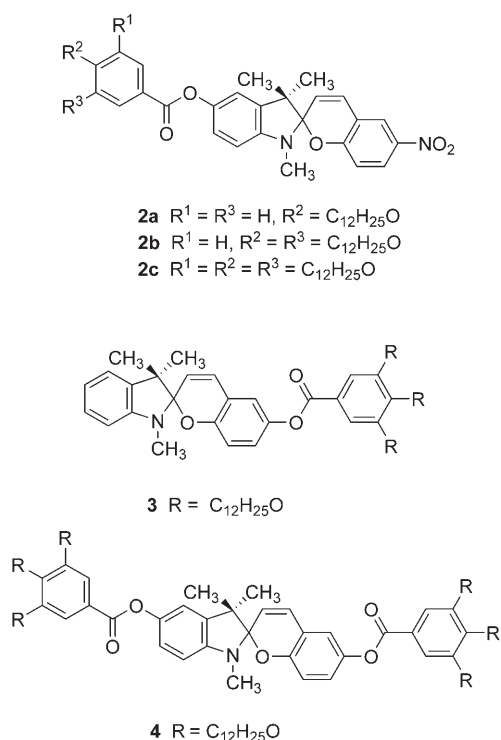

Scheme 1. Molecular structure of compound **1**.

acid formed columnar phases due to acid-induced spiro–merocyanine isomerization of **1**.

In the present study, we studied the acid-induced LC properties of a number of spiropyran derivatives **2–4** (Scheme 2) with different molecular shapes. Compounds **2a–c** have one, two, and three dodecyloxy chains connected to the phenyl moiety, respectively, whereas compounds **3** and **4** have one or two fan-shaped benzoate moieties attached to the different locations of the spiropyran core. It is known that molecular shape is a major factor in determining the mesophase morphologies of low-mass thermotropic liquid crystals.[9] The LC properties of the series of compounds **2–4** should be greatly affected by a change in the number of dodecyloxy chains on a phenyl ring or the positions of the fan-shaped benzoate moiety of the mesogenic molecules. These effects are due to the change in the volume fractions of mutually incompatible parts such as rigid/flexible or polar/nonpolar moieties combined in the same molecule.[2,10] We expected that smectic and columnar phases for this series of compounds **2–4** would be induced by the addition of acids. Furthermore, an induction of LC phases by UV irradiation for **2a–c**, which have a photoresponsive nitrospiropyran moiety, was expected because of the formation of ionic MC isomers. The MC isomers can form ordered nanostructures through ionic interactions. Thus, the ability to form LC phases of **2a–c** by photoisomerization alone was also examined.

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Scheme 2. Molecular structures of compounds **2–4**.

Results and Discussion

Molecular Design

Compounds **2a–c** have a nitro substituent onto the 6′-position of the benzopyran ring. For these nitro compounds, enhancement of photochromic properties was expected.[11] These compounds have no flexible linker between the spiropyran and the benzoate moieties because our preliminary studies indicated that the thermal stability of the LC phases was improved by removing this linker.[12] Compounds **2** and **3** have a benzoate group with dodecyloxy chains at different positions of the spiropyran moiety, whereas **4** has two benzoate groups attached to the spiropyran moiety.

Liquid-Crystalline Properties

The induction of the LC phases of compounds **2–4** was expected to occur by a) the addition of an acid and b) photoir-

radiation of the nitrospiropyran (**2a–c**) in the bulk liquid states. The two different approaches to the induction of mesomorphism for **2a–c** are shown schematically in Scheme 3.
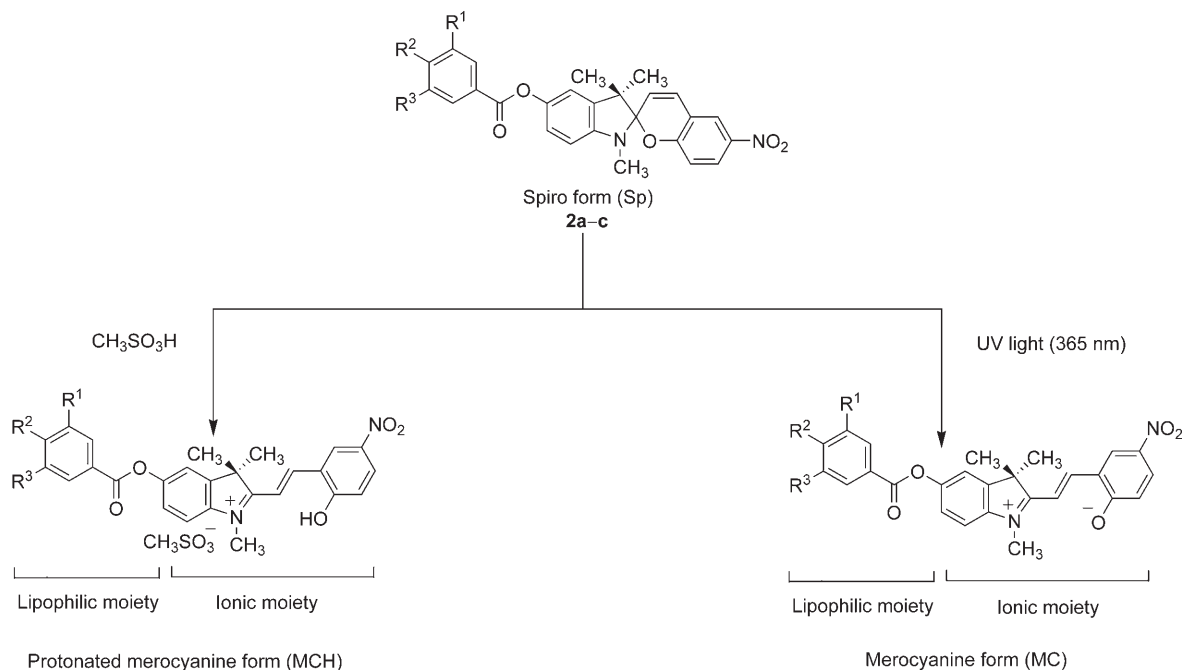
Acid-Induced LC Formation

For acid-induced LC formation, methanesulfonic acid (CH_3SO_3H) was selected because it is a strong protonic acid and has a low melting point (18 °C) and vapor pressure. The selection of an acid with a low melting point was expected to be especially critical for the formation of room-temperature LC materials in a system of a binary mixture. The binary mixtures of **2–4** with CH_3SO_3H were prepared in solution form and were then dried in air overnight (see Supporting Information). The thermal properties of the single components of **2–4** and their equimolar mixtures with CH_3SO_3H are given in Table 1. The single components of **2–4** in the spiro form (Sp) did not show mesomorphism, whereas all equimolar mixtures of **2–4** with CH_3SO_3H exhibited enantiotropic LC phases due to the formation of the protonated merocyanine (MCH) isomers of **2–4**. The equimolar mixtures of **2a–c** with CH_3SO_3H were non-eutectic, whereas the equimolar mixtures of **3** and **4** with CH_3SO_3H were eutectic.[8,13] A binary mixture of **2a** and CH_3SO_3H (**2a**/CH_3SO_3H) showed an enantiotropic smectic A (SmA) phase. Figure 1 shows a typical texture of the SmA phase displayed by the mixture of **2a**/CH_3SO_3H at 105 °C upon cooling. Similarly, the mixture of **2b** and CH_3SO_3H also exhibited an SmA phase even though the two dodecyloxy chains might disturb the layered packing of **2b** (see Supporting Information). The X-ray diffraction pattern of **2a**/CH_3SO_3H at 105 °C indicates one distinct reflection in the small-angle region, which corresponds to the layer spacing $d = 46.9$ Å (Figure 2). In the case of **2b**/CH_3SO_3H, the X-ray diffraction pattern at 105 °C shows a sharp peak at $2\theta = 2.12°$, which corresponds to the layer spacing $d = 41.6$ Å (see Supporting Information). On the basis of the energy-minimized molecular conformation, the molecular length of **2a** in the stretched MCH form was calculated to be approxi-

Table 1. Thermal properties of compounds **2–4** in the bulk form and in equimolar mixtures with CH_3SO_3H.

Compound	Phase-transition behavior[a]
2a	Cr −3 (0.9) Iso
2b	Cr −5 (10.1) Iso
2c	Cr −7 (27.2) Iso
3	Cr$_1$ 24 (5.2) Cr$_2$ 59 (11.6) Iso
4	Cr 4 (17.2) Iso
2a/CH_3SO_3H	Cr 77 (3.5) Cr+SmA 94 (−)[b] SmA 119 (−)[b] Iso
2b/CH_3SO_3H	Cr 20 (4.3) Cr+SmA 75 (−)[b] SmA 192 (−)[b] Iso
2c/CH_3SO_3H	Cr −47 (7.8) Cr+Col$_h$ 12 (−)[b] Col$_h$ 135 (0.2) Iso
3/CH_3SO_3H	Cr 77 (3.5) Col$_h$ 140 (−)[b] Iso
4/CH_3SO_3H	Cr −40 (12.5) Col$_h$ 124 (−)[b] Iso

[a] Transition temperatures (°C) and enthalpy changes (kJ mol^{-1}, in parentheses) were determined by differential scanning calorimetry (DSC). [b] The transition enthalpies were not detected by DSC. Cr = crystalline, SmA = smectic A, Cr+SmA = a biphasic mixture of crystalline and smectic A, Col$_h$ = hexagonal columnar, Cr+Col$_h$ = a biphasic mixture of crystalline and hexagonal columnar, Iso = isotropic.

Abstract in Japanese:

メタンスルホン酸の付加により開環してスメクチック A 液晶相あるいはカラムナー液晶相を示すスピロピラン化合物を合成した。これらの化合物は酸の付加によりメロシアニン環構造を形成していることが紫外可視吸収スペクトルにより明らかになった。メロシアニン環とメタンスルホン酸の複合化したイオン部位と、脂肪族鎖および芳香環からなる非イオン部位のナノ相分離構造の形成が、液晶相の発現と安定化に寄与していると考えられる。これらのスピロピラン化合物は、紫外線照射による開環反応によっては液晶性を示さなかった。

Scheme 3. Schematic illustration of the acid- and photoinduced isomerizations of compounds **2a–c**.
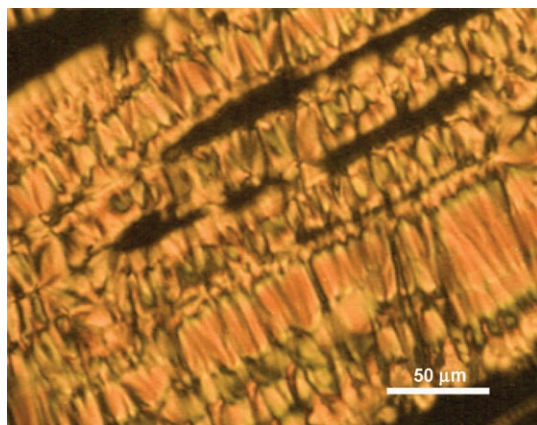
Figure 1. Polarized optical photomicrograph of an equimolar mixture of **2a**/CH₃SO₃H in the SmA phase at 105°C upon cooling.
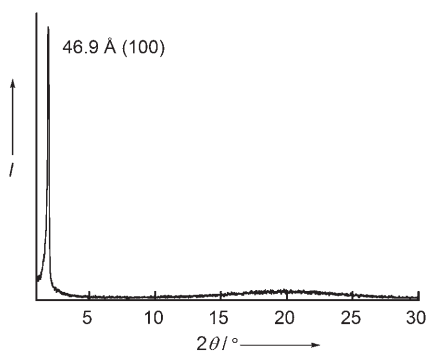
Figure 2. Wide-angle X-ray diffraction pattern of a binary mixture of **2a**/CH₃SO₃H in the SmA phase at 105°C.

mately 32.9 Å (see Supporting Information). The length of the aromatic core of **2a** was 17.1 Å, whereas the length of the fully extended aliphatic dodecyloxy chain was estimated to be 15.8 Å. These results suggest that the binary mixtures **2a**/CH₃SO₃H and **2b**/CH₃SO₃H form interdigitated bilayer structures.[14]

For the mixture **2c**/CH₃SO₃H, the LC phase was observed from 12 to 135°C (Table 1). Under observation with a polarized optical microscope at 25°C, the mixture showed the typical texture of the columnar phase (Figure 3). The equimolar mixture of **3**/CH₃SO₃H also formed a columnar phase from 77 to 140°C. For the mixture **4**/CH₃SO₃H, the columnar phase was observed from −40 to 124°C. The introduction of six flexible dodecyloxy chains on both sides of the spiropyran moiety suppresses the melting temperature of the equimolar mixture. The columnar structures of the binary mixtures of **2c**, **3**, and **4** with CH₃SO₃H have a hexagonal arrangement. For example, the small-angle X-ray scattering pattern (Figure 4) of the mixture **2c**/CH₃SO₃H at 25°C shows three Bragg reflections in the small-angle region with a d-value ratio of $1:1/\sqrt{3}:1/2$ ($d_{100}=44.6$ Å, $d_{110}=25.8$ Å, and $d_{200}=22.3$ Å), which corresponds to the reflections (100), (110), and (200). Compound **2c** in the MCH form has an ionic and rigid planar core as well as lipophilic flexible alkyl chains that are incompatible. As a result of their nanosegregation,[2] the MCH isomers of **2c** self-assemble into a one-dimensional columnar nanostructure in which the ionic moiety occupies the central part of the column stratum and the lipophilic dodecyloxy chains are arranged in the periphery of the column (Figure 5). The induction of the mesomorphism is due to the presence of ionic interactions[15,16] in the MCH isomers of **2c** in the center of the column stratum. Furthermore, the space filling of the meth-
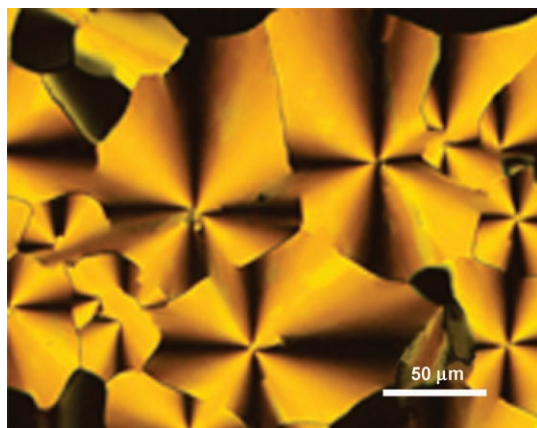
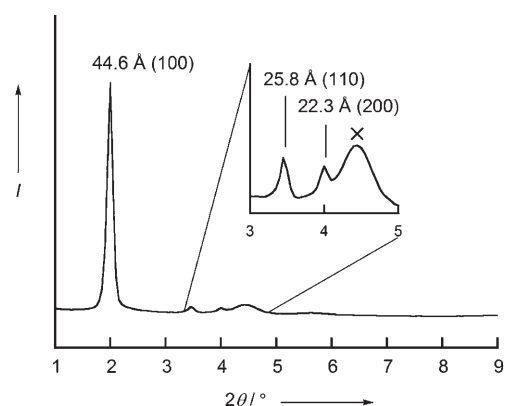Figure 3. Polarized optical photomicrograph of an equimolar mixture of **2c**/CH$_3$SO$_3$H in the columnar phase at 25 °C on cooling.

Figure 4. Small-angle X-ray scattering pattern of a binary mixture of **2c**/CH$_3$SO$_3$H in the columnar phase at 25 °C. The peak at 4.4° (×) corresponds to the diffraction due to the Kapton equipped in the X-ray instrument.

Figure 5. Possible interactions in the inner columnar parts in the self-assembled columnar nanostructures. The inner part consists of the cationic MCH form of **2c** and the methanesulfonate anion.
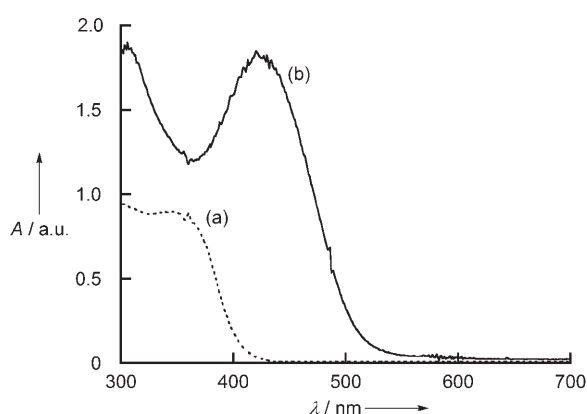
Figure 6. UV/Vis spectra of a) **2c** in the bulk liquid state and b) an equimolar mixture of **2c**/CH$_3$SO$_3$H in the columnar LC state at 25 °C.

anesulfonate anion in the center of the column stratum may also be important for the stabilization of the LC nanostructures of **2c** in the MCH form.

UV/Vis spectra of **2**–**4** were obtained to examine the formation of MCH isomers upon the addition of CH$_3$SO$_3$H. As these spectra show the same patterns, only the spectra of **2c** are presented. As shown in Figure 6, compound **2c** in the bulk liquid state at 25 °C shows an absorbance of $\lambda_{max} =$ 355 nm, which corresponds to the colorless closed-ring Sp form. Upon mixing with CH$_3$SO$_3$H at an equimolar ratio, an absorption band of $\lambda_{max} =$ 420 nm was observed. On the basis of previous reports,[6c,e,17] this absorption peak was ascribed to the formation of the MCH isomer. The absorption band of the MC isomer at 500–600 nm[4a,7c,e] was not detected. Thus, it was confirmed that only the MCH isomer is formed when **2c** is mixed with CH$_3$SO$_3$H.

Feasibility Study of Photoinduced LC Formation

We expected compound **2c** in the MC state to exhibit LC nanostructures. UV irradiation was performed for **2c**, and

UV/Vis spectra of **2c** in the solution and bulk liquid state were obtained. In THF (1×10^{-4} M), **2c** in the Sp form showed a broad absorption below 350 nm (see Supporting Information). Upon UV irradiation at room temperature (365 nm), new absorption peaks at 370 and 585 nm[18] for the MC isomer were observed. This change in UV absorption indicates the photoisomerization of **2c**. In the bulk liquid state, the color of **2c** changed immediately from light red to dark purple upon UV irradiation (see Supporting Information). The UV/Vis spectra of **2c** in the bulk liquid state at different irradiation times were collected (Figure 7). After

Figure 7. UV/Vis spectral variations of **2c** in the bulk liquid state during UV irradiation (365 nm) for 20 min at intervals of 2 min at 25 °C.

UV irradiation, the UV/Vis spectrum of **2c** in the bulk liquid state showed the absorption peaks at 380 and 550 nm of the MC isomer.[19] The absorption of the MC isomer of **2c** reached the satu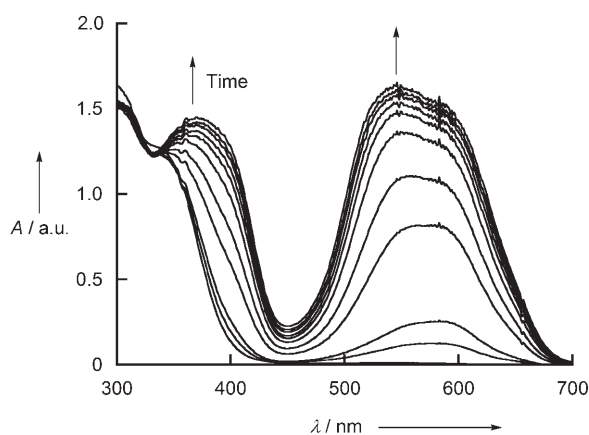ration value after photoirradiation for 20 min. Under observation with a polarized optical microscope, no birefringence was detected for **2c** during UV irradiation for up to 1 h (see Supporting Information). The conversion of the spiro–merocyanine isomerization of **2c** was observed by Fourier transform infrared (FTIR) spectroscopy (see Supporting Information). The IR absorption bands of the Sp and MC isomers were assigned previously.[20,21] The conversion was estimated to be about 85 % by quantifying the spectral change of the absorption of the alkene C=C stretching band for the Sp isomer at 1650 cm^{-1} (see Supporting Information). Interestingly, the MC form of **2c** obtained by UV irradiation does not lead to the formation of the mesophases even though the MC isomers tend to form stacked molecular aggregates through ionic interactions in the solid state.[4,22] It is assumed that the formation of ionic interactions for the single components of the MC isomers is not suitable for the induction of the mesophase. In contrast, for the complex of the MC form of **2c** and methanesulfonic acid, the stable mesophase was obtained. This acid-induced mesomorphism is due to the formation of ionic interactions that are suitable for the formation of the LC nanosegregated structures.[15,16,23] Moreover, the existence of the acid molecule can effectively stabilize the mesophase due to the filling of the space.

Hydrogen bonding[2a–c,24] may also contribute to the formation of the mesophase for the complex of the MC form of **2c** and methanesulfonic acid. Ikkala and co-workers pointed out that hydrogen bonding may be formed between a phenolic residue and the methanesulfonate anion in the mesophase, although the FTIR spectral features did not indicate the presence of the hydrogen bonding.[25] On the other hand, a previous single-crystal X-ray study on a binary mixture of a nitrospiropyran with trifluoroacetic acid suggested the possible formation of hydrogen bonding between the phenolic OH group and the trifluoroacetate anion in the MCH isomer.[26]

Conclusions

A new family of LC materials based on spiropyran has been developed. Acid-induced spiro-protonated merocyanine isomerization was used to induce mesomorphism. Layered and columnar LC assemblies of the binary mixtures consisting of the spiropyran derivatives and methanesulfonic acid were formed. The LC structures are dependent on the number of long alkyl chains. On the other hand, no mesophase was formed upon photoirradiation of the spiropyran compounds. The induction of the LC nanostructures for the complex of the MC form and methanesulfonic acid is due to the formation of ionic interactions and the nanosegregation of ionic and nonionic parts. Moreover, the filling of the space by the methanesulfonate anion is important for the stabilization of the LC nanostructures. This paper shows an interesting approach to the development of stimuli-induced thermotropic liquid crystals based on spiropyrans. They can potentially be used as one-dimensional ion conductors and acid sensors.

Experimental Section

General

All reagents were purchased from Tokyo Kasei, Aldrich, and Wako. They were used as received without purification. Analytical thin-layer chromatography (TLC) was performed on a silica-gel plate from E. Merck (silica gel F$_{254}$). Silica-gel column chromatography was carried out with silica gel 60 from Kanto Chemical (spherical 40–50 μm). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer with CDCl$_3$. ^{1}H and ^{13}C chemical shifts (δ) are expressed in ppm with Me$_4$Si as an internal standard. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were collected on a PerSpective Biosystem voyager DE STR spectrometer. Elemental analysis was performed on a Yanaco MT6-CHN autocorder. DSC was performed with a NETZSCH DSC204 Phoenix instrument at a scanning rate of 2 °C min^{-1}. An Olympus BX51 polarizing optical microscope equipped with a Mettler FP82 HT hot stage was used for texture observation of the LC phases. Transition temperatures were determined at the onset of transition peaks on the second heating and by visual observation under the polarized optical microscope. Wide-angle X-ray diffraction (WAXD) patterns were obtained by using a Rigaku RINT-2500 system with monochromated Cu$_{K\alpha}$ irradiation. Two-dimensional small-angle X-ray scattering (2D SAXS) patterns were recorded with an image plate detector (R-AXIS DS3C). Absorption spectra were recorded on an Agilent (model 8453) UV/Vis spectrophotometer in a 1-cm quartz cell for samples in tetrahydrofuran. UV irradiation was carried out by using a high-pressure mercury lamp (Ushio, 500 W) with a glass filter (Asahi Techno-glass UVD-36C) as an irradiation source. A sandwiched quartz cell was used for UV/Vis spectroscopy of samples in the bulk state. The energy-minimized molecular conformation of each compound **2a–c** was obtained under the COMPASS force field by means of the Discover 3 module of MS modelling (version 4.0; Accelrys, Inc.).

Photoirradiation Experiment

A sample of **2c** in the bulk liquid state was sandwiched between two quartz substrates. The thickness of the sample was fixed at 2 μm by a spacer of silica beads. The samples were exposed to UV light at 365 nm (22 mW cm^{-2}).

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