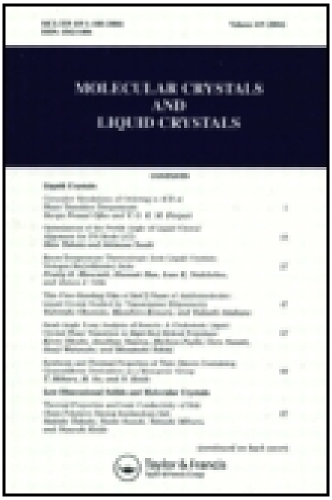


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

J-Aggregate Formation of Spiropyran Derivatives in LB and Vapor-Deposited Thin Films

Kouji Matsumoto [a] , Takashi Shinohara [a] , Yasuko Koshiba [a] , Yasukiyo Ueda [a] & Zhenguo Ji [b]
[a] Graduate School of Science and Technology, Kobe University , Rokko, Nada, Kobe, Japan
[b] Zhejiang University , China

To cite this article: Kouji Matsumoto , Takashi Shinohara , Yasuko Koshiba , Yasukiyo Ueda & Zhenguo Ji (2006) J-Aggregate Formation of Spiropyran Derivatives in LB and Vapor-Deposited Thin Films, Molecular Crystals and Liquid Crystals, 445:1, 17/[307]-26/[316], DOI: 10.1080/15421400500366753

To link to this article: http://dx.doi.org/10.1080/15421400500366753

Mol. Cryst. Liq. Cryst., Vol. 445, pp. 17/[307]–26/[316], 2006
Copyright © Taylor & Francis LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500366753

J-Aggregate Formation of Spiropyran Derivatives in LB and Vapor-Deposited Thin Films

Kouji Matsumoto
Takashi Shinohara
Yasuko Koshiba
Yasukiyo Ueda
Graduate School of Science and Technology, Kobe University, Rokko, Nada, Kobe, Japan

Zhenguo Ji
Zhejiang University, China

J-aggregate formation in the films of spiropyran derivatives (SP1822 and SP18) prepared with Langumuir-Blodegett (LB) and vapor-deposition methods was investigated. In the films of SP1822, J-aggregate formation occurred with UV light illumination and thermal treatment. In the case of SP18 film, on the other hand, only photoisomerization occurred. When the PMC-form of SP18 was transferred onto a glass plate, J-like aggregate formation occurred after UV light illumination. By UV light illumination during evaporation process, SP1822 formed J-aggregate. Finally, SP1822 J-aggregate film oriented one-dimensionally was fabricated by using a PTFE layer as a substrate.

Keywords: J-aggregate; J-like aggregate; LB method; photochromic behavior; spiropyran; vapor-deposition method

This work was partially supported by a Grant-in-Aid for Scientific Research (B) (No. 16360040) from the Japan Society for the Promotion of Science. This work was also supported by the Tokyo Ohka Foundation for the Promotion of Science and Technology and by the Photonics Materials Laboratory Project of the VBL of the Graduate School of Science and Technology, Kobe University.

Address correspondence to Yasukiyo Ueda, Graduate School of Science and Technology, Kobe University, Rokko, Nada, Kobe 657-8501, Japan. E-mail: yueda@kobe-u.ac.jp

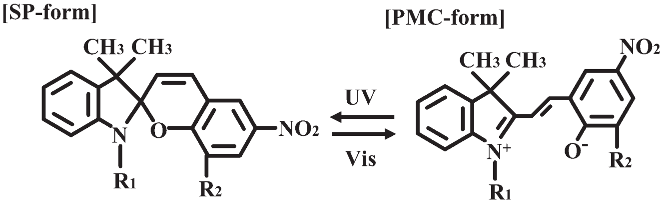
INTRODUCTION

J-aggregates are assemblies of organic dye molecules with an ordered structure. The typical feature of J-aggregates is the red-shift of the absorption band with a small Stokes shift. J-aggregate has been attracted wide attention. Interests in J-aggregates originally stemmed from the spectral sensitization. Recent development in the research on J-aggregates derives from the expectations that J-aggregate will be used as materials for optical storage and ultrafast optical switching. Spiropyran is one of the dye molecules that form J-aggregates. Spiropyran derivatives reversibly isomerize between spiropyran (SP)-form and photomerocyanine (PMC)-form by UV light illumination. Some PMC-form molecules assemble spontaneously in J-aggregate. There have been many reports on photochromic behavior and J-aggregate formation of spiropyran derivatives [1–5]. Previously, we reported J-aggregate formation of SP1822 in LB and vapor-deposited film [6]. J-aggregate formation in SP1822 LB film occurred by UV light illumination at 35°C.

In this study, the LB films of SP18 and of SP1822/SP18 mixture were fabricated and J-aggregate formation in the LB film was investigated. SP1822 was also vapor-deposited on its J-aggregate LB film and a friction-transferred polytetrafluoroethylene (PTFE) layer. The effects of substrates and the vapor-deposition process on J-aggregate formation were investigated.

EXPERIMENTAL

Glass plates were used as a substrate for preparation of LB films. They were cleaned ultrasonically in water with detergent for 15 minutes, in distilled water for 15 minutes, and in methanol for 15 minutes. Two spiropyran derivatives used here were 1-octadecyl-3,3-dimethyl-6-nitro-8-[docosanoyloxymethyl]-spiro[2H-1-benzopyran-2,2-indoline] (SP1822) and 1′,3′-dihydro-3′,3′-dimethyl-6-nitro-1′-octadecylspiro[2H-benzopyran-2,2′-2H] indole (SP18). Their molecular structures and photochromic behavior are shown in Figure 1. These samples were purchased from Dojindo Laboratory Co. Lt. LB films of spiropyran derivatives were prepared on air-water interface of a LB through (Kyowa Kaimen Kagaku Co. Lt). A chloroform solution of SP1822 or SP18 mixed with arachidic acid (AA) and of SP1822/SP18/AA mixture (molar ratio = 1:1 and 1:1:1, respectively) was spread on a distilled water kept at 5°C. The molecules were compressed with a moving barrier at the speed of 14 $\mathrm{cm^2 min^{-1}}$. Layers were transferred onto glass plates by vertical dipping method. Vapor-deposition of SP1822 was



SP18 :$R_1=C_{18}H_{37}$ $R_2=H$
SP1822 :$R_1=C_{18}H_{37}$ $R_2=CH_2OCOC_{21}H_{43}$

FIGURE 1 Molecular structure and photochromism of spiropyran derivatives.

performed as follows. SP1822 was evaporated on a substrate from fused silica crucible heated by a tungsten filament in a vacuum of 10^{-3} Pa. A glass plate, SP1822 LB film and a friction-transferred PTFE layer were used as a substrate. The substrate temperature was kept at room temperature (r.t.) and 35°C and the deposition rate was controlled to be about 1 nm min^{-1} in thickness monitored by a quartz crystal microbalance. The film thickness was about 20 nm. When the UV light was illuminated during evaporation process, the light intensity was controlled to be about 5 μW cm^{-2} and 15 μW cm^{-2}. The optical properties and structures of the films were investigated by visible absorption and photoluminescence spectroscopy and transmission electron microscopy (TEM).

RESULTS AND DISCUSSION

LB Film

SP18 and SP1822 LB films were consisted of SP-form molecules because these films had no absorption peaks in the visible wavelength range. Figure 2 shows the spectral changes of SP18 and SP1822 LB films with UV light (365 nm) illumination. Upon UV light illumination at room temperature, the broad absorption band appeared in the wavelength range of 450–650 nm, as shown in Figure 2(a). This band is assigned to PMC-form of SP1822 molecule. When the SP1822 LB film was exposed to UV light at ambient temperature of 35°C, the red-shifted sharp absorption peak appeared at 618 nm in addition to absorption peak of PMC-form, as shown in Figure 2(b). In fluorescence spectrum of the film, a single emission peak was observed at 624 nm (Fig. 2(c)). The Stokes shift was 6 nm. From these results, this band is assigned to J-aggregate of PMC-form. In SP18 LB film, on the other hand, only photoisomerization from SP-form to PMC-form occurred.

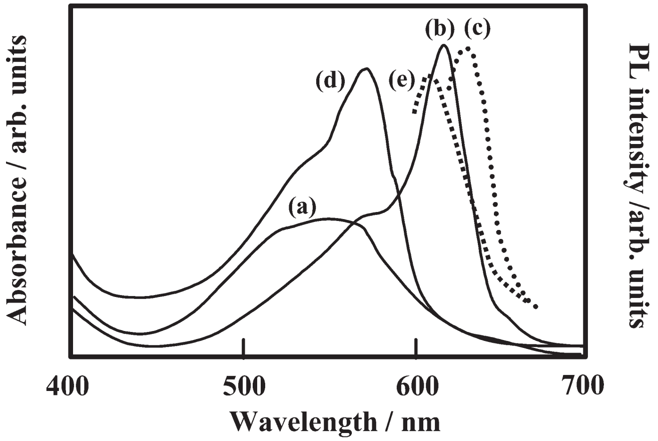


FIGURE 2 Visible absorption (solid lines) and PL (dotted lines) spectra of the LB films of SP1822 (a,b,c) and SP18 (d,e) after UV light illumination at r.t. (a), 35°C (b,c) and 50°C (d,e).

Another process is necessary for J-aggregate formation of SP18. Prior to spreading on water, SP18 was exposed to UV light in chloroform solution. SP18 changed from SP-form into PMC-form. The solution containing PMC-form was spread on water and the film was transferred onto a glass plate. After UV light illumination at ambient temperature of 50°C, the red-shifted sharp absorption peak appeared at 570 nm, as shown in Figure 2(d). Single emission peak was observed at 605 nm (Fig. 2(e)). The Stokes shift between the absorption peak and the emission peak was 35 nm. Generally, J-aggregate is characterized with a small Stokes shift (less than 10 nm). The absorption band at 570 nm is assigned not to J-aggregate of PMC-form but to different aggregate. Therefore, this band is assigned as J-like aggregate. Figure 3 shows the absorption spectra of the LB film of a SP1822/SP18 mixture after UV light (365 nm) illumination. Upon UV light illumination at ambient temperature of 30°C, two absorption peaks appeared at 570 nm and 618 nm in the absorption spectrum of the film (Fig. 3(a)). The absorption peaks at 570 nm and 618 nm are assigned to J-like aggregate of SP18 and J-aggregate of SP1822, respectively. With longer UV light illumination, the intensity of absorption peak at 618 nm became remarkably strong, but the intensity change of absorption peak at 570 nm was not so large comparing with that of absorption peak at 618 nm. Upon UV light illumination at 50°C, on the other hand, the absorption peak appeared only at 570 nm, as shown in Figure 3(b). These results indicate that J-aggregate and

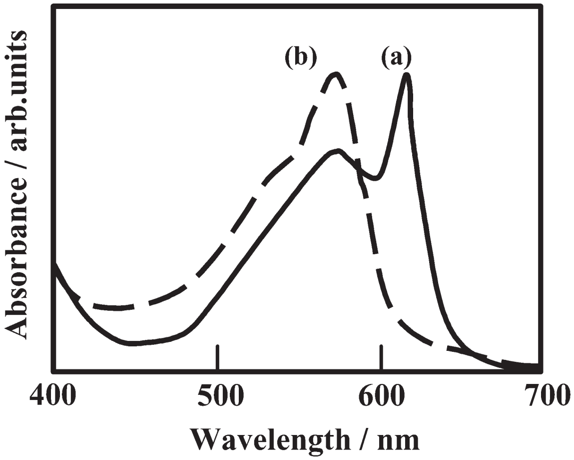


FIGURE 3 Visible absorption spectra of the LB film of SP1822/SP18 mixture after UV light illumination at 30°C (a) and 50°C (b) for 15 min.

J-like aggregate formation in the LB film of SP1822/SP18 mixture occurred selectively depending on the ambient temperature during UV light illumination.

Vapor-Deposited Film

SP1822 was vapor-deposited on a glass plate without any thermal decomposition. The deposited film was composed of SP-form molecules. After UV light illumination at room temperature, the broad absorption band corresponding to PMC-form appeared in the wavelength range of 500–600 nm. The photoisomerization from SP-form to PMC-form occurred easily even in a vapor-deposited film. When the film was exposed to UV light under the ambient temperature at 35°C, J-band appeared at 618 nm. J-aggregation in the vapor-deposited film occurred under the condition of UV light illumination at slightly high temperature than r.t. (i.e., 35°C). Figure 4 shows the absorption spectra of SP1822 film vapor-deposited on SP1822 J-aggregate LB film before and after UV light illumination. The absorption spectrum of the deposited film shows two peaks at 570 nm and 618 nm (Fig. 4(a)). These peaks originate from PMC-form and J-aggregation in LB film used as a substrate, respectively. It is noticed that J-aggregate is stable in a vacuum. After UV light illumination without special heating, the intensities of both absorption peaks increase (Fig. 4(b)). It was found that J-aggregation is induced

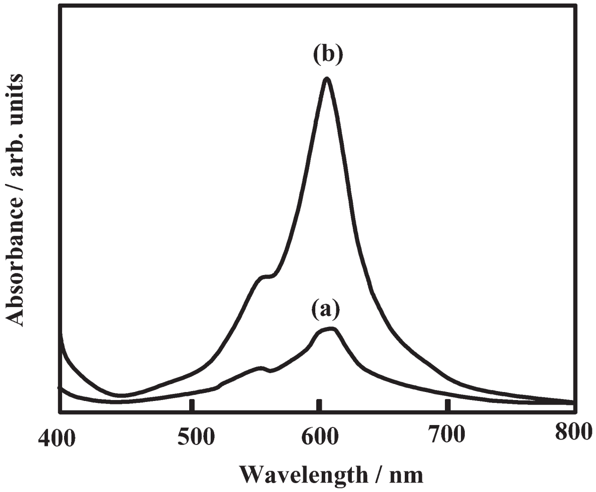


FIGURE 4 Visible absorption spectra of the SP1822 film vapor-deposited on SP1822 J-aggregate LB film before (a) and after (b) UV light illumination at r.t.

only with UV light illumination in this case. It is noteworthy that the intensity ratio of I_{570}/I_{620} is same before and after UV light illumination. There are two domains in SP1822 LB film. One is consisted of PMC-form and the other is J-aggregate of PMC-form, as shown in Figure 5(a). Evaporant molecules were deposited as SP-form (Fig. 5(b)). Upon UV exposure, SP-form molecules photoisomerize to PMC-form. At that time, SP-form molecules on the domain consisted of PMC-form only photoisomerize. SP-form molecules on the domain consisted of J-aggregate of PMC-form, on the other hand, photoisomerize and assemble spontaneously since the J-aggregate domain acts as a nucleus for aggregate formation, as shown in Figure 5(c). Therefore, both domains coexist in the film and the ratio of PMC-form/J-aggregate is same value before and after UV light illumination. J-aggregate formation induced only with UV light illumination (without special heating) in the vapor-deposited film was observed for the first time. This result suggests that J-aggregate formation is dependent strongly on the substrate structure.

Since pioneering research by Wittmann and Smith, the usefulness of a friction-transferred PTFE layer as a substrate for achieving high molecular alignment has been attracted wide attention. We have investigated the structure and properties of organic molecules such as phthalocyanine and distyrylbenzene and so on [7–11]. Such molecules oriented uniaxially on a PTFE layer and their optical and electric

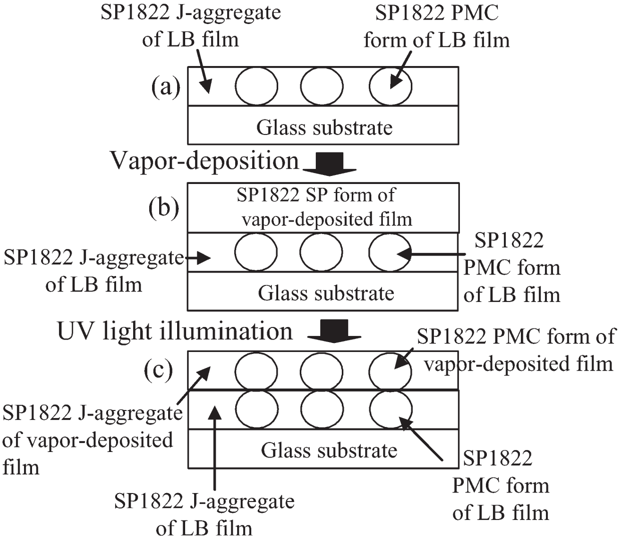


FIGURE 5 Schematic representation of J-aggregate formation of evaporant SP1822 deposited on its LB film.

properties indicated remarkable anisotropy. In this study, SP1822 was deposited on a PTFE layer with UV light illumination during evaporation process. Figure 6 shows the experimental setup and absorption spectra of SP1822 film vapor-deposited on a PTFE layer. The SP1822 film deposited on a PTFE layer without UV light illumination also was consisted of SP-form molecules. After UV exposure under the ambient temperature at 35°C, J-band appeared at 618 nm, as shown in Figure 6(a). The full width at half maximum (FWHM) of absorption peak is 52 nm. When SP1822 was deposited at 35°C under UV light illumination (365 nm, 15 μWcm^{-2}) during evaporation process, a sharp absorption peak corresponding to J-aggregate of PMC-form appeared just after vapor-deposition, as shown in Figure 5(b). This indicates that the J-aggregate formation occurred during vapor-deposition process. The FWHM of J-band peak was 28 nm. On the other hand, the FWHM of J-band peak of the film deposited under UV light illumination with 5 μWcm^{-2} power is 40 nm. Generally, the FWHM relates closely with molecular ordering in the film. The more the regularity of molecular packing in the film improves, the narrower the FWHM becomes. Therefore it is found that the regularity of molecular packing in J-aggregate also depends on the UV light power during evaporation. Figure 7 shows a TEM image and a high resolution electron diffraction

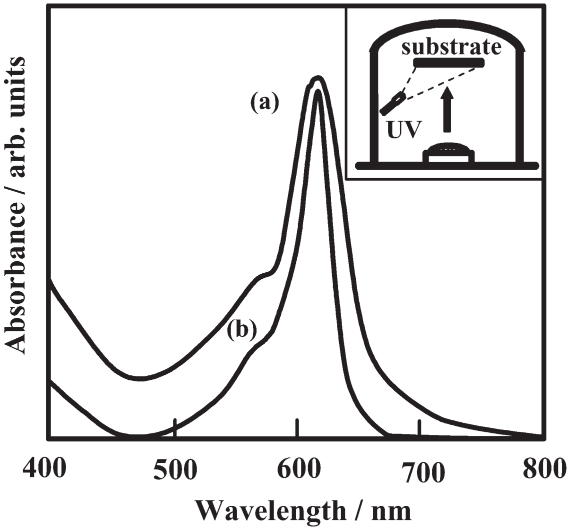


FIGURE 6 Visible absorption spectra of the SP1822 film vapor deposited on a PTFE layer (a) Exposed to UV light at 35°C after vapor-deposition (b) With UV light illumination at 35°C during vapor-deposition. The inset indicates the schematic diagram of experimental setup.

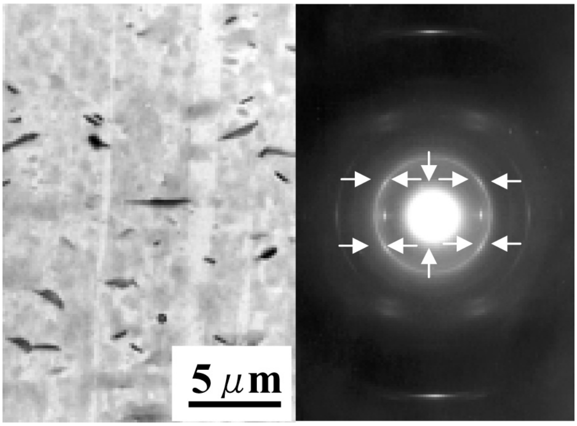


FIGURE 7 TEM image and HRED pattern of the SP1822 film vapor-deposited on a PTFE layer with UV light illumination during evaporation process.

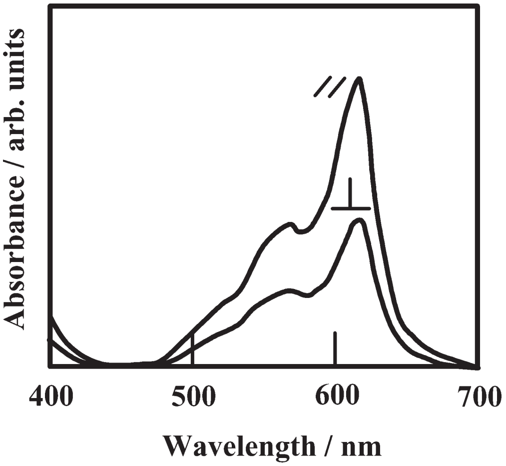


FIGURE 8 Visible polarized absorption spectra of the SP1822 film vapor-deposited on a PTFE layer with UV light illumination during evaporation process.

(HRED) pattern of the film vapor-deposited on a PTFE layer at 35°C with UV light illumination during evaporation process. The film was composed of thin plate-like crystals and rod-like ones. The HRED pattern of the film shows the superposition of the reflection spots from the PTFE layer used as a substrate and those from the deposited J-aggregate indicated by white arrows in the figure. The reflection spots from the deposited J-aggregate appear as arc. This suggests that J-aggregate oriented one-dimensionally on a PTFE layer. However, further information concerning the molecular orientation can not be obtained because the crystal structure of J-aggregate of PMC-form has not been determined yet. Figure 8 shows the polarized absorption spectra of the film on a PTFE layer. The anisotropic feature in absoption can be observed. The dichroic ratio ($I_{\parallel}/I_{\perp}$) obtained from absorption peak at 618 nm is 2.1. This is the first report on fabrication of one-dimensionally oriented J-aggregate originated from spiropyran derivatives.

CONCLUSIONS

This report provides the detailed results of J-aggregate formation in LB and vapor-deposited films of spiropyran derivatives. In SP1822 films prepared with both LB and Vapor-deposition methods, J-aggregate formation occurred with UV light illumination at 35°C. In the case of SP18 film, only photoisomerization occurred. When the PMC-form of

SP18 was transferred onto a glass plate, J-like aggregate formation occurred after UV light illumination at 50°C. In the LB film of SP1822/SP18 mixture, on the other hand, J-aggregate and J-like aggregate formation occurred selectively depending on the ambient temperature during UV light illumination. SP1822 vapor-deposited on its J-aggregate LB film formed J-aggregate only with UV light illumination (without special heating). This is the first experimental result that J-aggregate formation in the vapor-deposited film was induced only with UV light illumination.

By UV light illumination during evaporation process, SP1822 formed J-aggregate. The FWHM at J-band peak of the film was much smaller than that of the film exposed to UV light at 35°C after vapor-deposition. Finally, SP1822 J-aggregate film oriented one-dimensionally was fabricated using a PTFE layer as a substrate.

REFERENCES

[1] Matsumoto, M. (2003). *J. Photochem. Photobio. A: Chemistry*, *158* (2–3), 199.
[2] Tachibana, H., Yamanaka, Y., Sakai, H., Abe, M., & Matsumoto, M. (2000). *J. Luminescence*, *87–89*, 800.
[3] Ando, E., Miyazaki, J., Morimoto, K., Nakahara, H., & Fukuda, K. (1985). *Thin Solid Films*, *133*, 21.
[4] Ueda, Y. & Nitta, K. (2001). *Jpn. J. Appl. Phys.*, *40*, 6951.
[5] Aritoshi, Y., Nitta, K., Ueda, Y., & Ji, Z. (2002). *Mol. Cryst. Liq. Cryst.*, *377*, 145.
[6] Nishitani, S., Shinohara, T., Koshiba, Y., Ueda, Y., & Ji, Z. (2004). *Mem. Grad. School Sci. & Technol., Kobe Univ.*, *22-A*, 33.
[7] Ueda, Y., Kuriyama, T., Hari, T., & Ashida, M. (1994). *J. Electron Microsc.*, *43*, 99.
[8] Ueda, Y., Kuriyama, T., Hari, T., Watanabe, M., Jingping, N., Hattori, Y., Uenishi, N., & Uemiya, T. (1995). *Jpn. J. Appl. Phys.*, *34*, 3876.
[9] Ueda, Y., Hari, T., Thumori, T., Yano, M., & Jingping, N. (1997). *Appl. Surface Sci.*, *113/114*, 304.
[10] Ueda, Y., Murakami, T., Masaki, S., Chen, J., Jingping, Ni., Yoshida, Y., Tanigaki, N., Yase, K., & Wang, D. K. (2001). *Mol. Cryst. Liq. Cryst.*, *370*, 245.
[11] Saito, T., Ueda, Y., Harada, K., & Fukunishi, K. (2003). *Mol. Cryst. Liq. Cryst.*, *407*, 157.