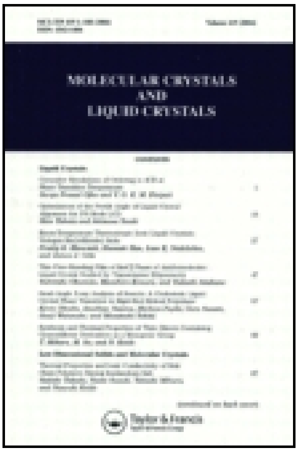

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photo-Oriented Trisazobenzene Layers for Patterned Liquid-Crystal Alignment

Pascal Wolfer [a] [f], Klaus Kreger [b] [c], Hans-werner Schmidt [b] [c], Natalie Stingelin [a] [d] [e] & Paul Smith [a] [e]

[a] Department of Materials, ETH Zürich, Zürich, Switzerland

[b] Macromolecular Chemistry I, University of Bayreuth, Bayreuth, Germany

[c] Bayreuther Institut für Makromolekülforschung (BIMF), University of Bayreuth, Bayreuth, Germany

[d] Department of Materials, Imperial College London, London, UK

[e] Centre for Plastic Electronics, Imperial College London, London, UK

[f] Pascal Wolfer, Centre for Organic Photonics and Electronics (COPE) the University of Queensland, Level 9, Chemistry Building, Imperial College London, St Lucia, QLD 4072, Australia

Version of record first published: 30 Jul 2012.

To cite this article: Pascal Wolfer , Klaus Kreger , Hans-werner Schmidt , Natalie Stingelin & Paul Smith (2012): Photo-Oriented Trisazobenzene Layers for Patterned Liquid-Crystal Alignment, Molecular Crystals and Liquid Crystals, 562:1, 133-140

To link to this article: http://dx.doi.org/10.1080/15421406.2012.674857

Mol. Cryst. Liq. Cryst., Vol. 562: pp. 133–140, 2012
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.674857

Photo-Oriented Trisazobenzene Layers for Patterned Liquid-Crystal Alignment

PASCAL WOLFER,[1,*,†] KLAUS KREGER,[2,3] HANS-WERNER SCHMIDT,[2,3] NATALIE STINGELIN,[1,4,5] AND PAUL SMITH[1,5]

[1]Department of Materials, ETH Zürich, Zürich, Switzerland
[2]Macromolecular Chemistry I, University of Bayreuth, Bayreuth, Germany
[3]Bayreuther Institut für Makromolekülforschung (BIMF), University of Bayreuth, Bayreuth, Germany
[4]Department of Materials, Imperial College London, London, UK
[5]Centre for Plastic Electronics, Imperial College London, London, UK

Photosensitive trisazobenzene-based layers, after irradiation with polarized light, are employed to align the common liquid-crystal (LC) compound 4-cyano-4′-heptylbiphenyl (7CB) into predetermined patterns. Surface analysis of the trisazobenzene films indicate that ordering of the LC material is not caused by illumination-induced surface relief structures, but through "molecular mesoepitaxial" phenomena. This finding can be exploited to produce in one-step in-plane patterns of randomly oriented and ordered macroscopic LC domains by irradiation of the substrates.

Keywords Azobenzene derivatives; cyanobiphenyl; liquid crystal cells; orientation layer; photo-induced alignment

1. Introduction

Since the discovery that azoxyanisole in its liquid-crystalline (LC) phase can be oriented simply by placing this compound between two sheets of mica [1], numerous alignment substrates have been advanced, including rubbed or buffed surfaces of certain polymers such as polyimide (PI) [2–9], microgrooved surfaces [10–12], or highly oriented thin films of poly(tetrafluoroethylene) (PTFE) [13,14]. The relevance of alignment layers, and developing pathways for inducing order in LC substances based on such structures, cannot be overestimated. This is self-evident in, for instance, the display industry where they allow efficient fabrication of homogeneously oriented structures for use in liquid-crystal displays (LCDs) [15–18]. There remains, however, a need for substrates comprising no topological features since these can lead to electrical shorts and often make use of relatively thick active layers a necessity. In addition, systems that enable straightforward patterning of the functional components into multidomain architectures are still much sought-after.

---

[*] Address correspondence to Pascal Wolfer, Department of Materials, ETH Zürich CH-8093, Zürich, Switzerland. E-mail: p.wolfer@uq.edu.au

[†] Current address: Pascal Wolfer, Centre for Organic Photonics and Electronics (COPE), the University of Queensland, Level 9, Chemistry Building, St Lucia QLD 4072, Australia.

Here, we explored application of films of small-molecular trisazobenzene derivatives for this purpose since the use of photosensitive species, such as photopolymers [19–23] or azobenzene-containing compounds [24–31], has been demonstrated to potentially provide a viable strategy toward layers that induce order/orientation only at predefined locations. Advantages that trisazobenzenes promise over the latter compounds are that some of the derivatives can readily be synthesized and purified, be either evaporated or cast from solution into films, thus, providing a versatile processing platform; and, furthermore, the resulting structures can be photo-aligned into controlled patterns by exposure to linearly polarized light–as we have shown recently in the fabrication of holographic gratings with them [32,33].

From the broad range of trisazobenzene derivatives previously studied, we selected 1,3,5-tris{[6-[4-[(4-methoxyphenyl)azo]phenoxy]-hexanoyl]amino}benzene (**1**) (chemical structure in Fig. 1a) for its convenient thermal and optical characteristics [32,33]. The common compound 4-cyano-4′-heptylbiphenyl [4,34,35] (7CB; Fig. 1a), with a nematic LC phase at ambient allowing straightforward deposition at room temperature [36], was employed as a model LC substance, to scrutinize the alignment-inducing capability of the trisazobenzenes.

2. Materials and Methods

2.1 Materials

The synthesis and characterization of trisazobenzene derivative **1** is described elsewhere [32]. 4-Cyano-4′-heptylbiphenyl (7CB) was purchased from Frinton Laboratories, Inc., Vineland, NJ, USA, and used as received. Tetrahydrofuran (THF) was acquired from Acros, Geel, Belgium, and dried over a molecular sieve.

2.2 Preparation of Thin Films and Liquid-Crystal Cells

Thin films of compound **1** were spin-cast at ambient with a Laurell WS-400B-6NPP/LITE spin-coater at 800 rpm from ∼1 wt% solutions in THF onto glass slides for optical microscopy and surface analysis, and onto polished sodium chloride discs for infrared spectroscopy. Typical thicknesses of the layers of **1** were in the range from 300 nm to 400 nm.

For assembling LC cells with the different trisazobenzene-coated substrates, a UV-curable adhesive (MasterBond UV15-7, MasterBond, Hackensack, NJ) was employed, to which 18 μm-sized glass spacer beads were added to define the cell thickness. The assembly was exposed for 4 min to the UV-light of a UVP, Blak-Ray Long Wave Ultraviolet Lamp, Model B 100 AP for complete curing of the glue. The glue-free areas of the LC cells were thereby protected from the UV-light irradiation to avoid undesired UV-exposure of the trisazobenzene layers.

2.3 Photo-Alignment

Photo-induced alignment of the trisazobenzene layers in the LC cells was performed at ambient by exposing the empty cells during 2 hours to linearly polarized light in a box of the dimensions 25 × 85 × 40 cm, fitted with an Osram® S Luminux® 9 W/860 (Daylight) source. The distance between cell or glass substrates and lamp was 10 cm in all experiments. A Polaroid HN-32 sheet polarizer was placed on top of the cells. To inscribe patterns into the trisazobenzene layers, a shadow mask of 100 μm thickness featuring a linear grating

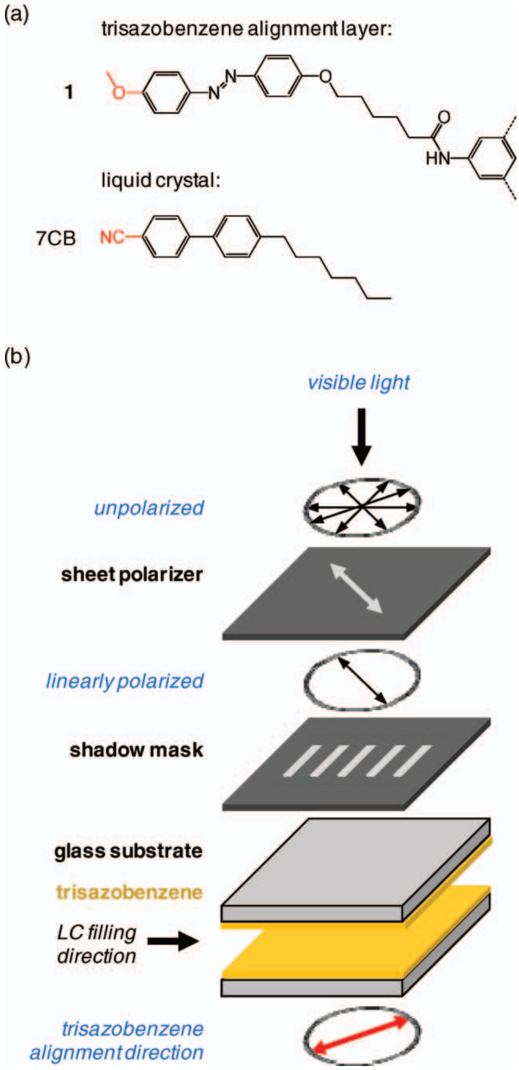

Figure 1. (a) Chemical structures of compounds employed. Functional groups analyzed with polarized infrared spectroscopy are highlighted in red (*cf*. Fig. 2a). (b) Schematic of the set up utilized for photo-induced patterning of trisazobenzene layers with linearly polarized light.

with slots of dimensions 100 × 5000 μm separated by 300 μm was positioned between the sheet polarizer and the LC cells (Fig. 1b).

2.4 Characterization

Optical microscopy was carried out with a Leica DM4000M polarizing light microscope.

Infrared (IR) spectra were recorded with a Bruker Vertex 70 spectrometer equipped with a Spectra-Tech IR polarizer. Scans were taken from 3000 cm^{-1} to 600 cm^{-1} before and after 2 hours illumination of empty LC cells with linearly polarized light, as well as of filled cells comprising photo-aligned trisazobenzene layers.

For scanning electron microscopy (SEM) analysis, substrates covered with thin films of compound **1** were coated with a thin conductive layer of platinum and images of irradiated and unexposed layers were recorded with a LEO 1530 Gemini microscope.

Atomic force microscopy (AFM) was performed with a Digital Instrument, Nano Scope IIIa, operating the device in the tapping mode. Fourier-transformed 2D patterns were calculated using MATLAB R2010a.

3. Results and Discussion

In order to explore the capability of compound **1** to orient LC materials when photo-aligned, glass and sodium chloride substrates were coated with the trisazobenzene derivative. Cells for alignment tests were assembled using two of such substrates and subsequently spatially patterned by partially illuminating them with linearly polarized light for 2 hours. To this end, we used a shadow mask featuring a linear grating. The light-polarization direction was chosen to be at an angle of 45° with respect to the axis of the linear grating, as depicted in Fig. 1(b). IR spectra were taken of empty cells constructed with the trisazobenzene-coated sodium chloride substrates to analyze if the trisazobenzene was photo-oriented in the illuminated areas. The corresponding spectra, recorded parallel and perpendicular to the light polarization direction, are presented in Fig. 2(a).

We observe a dichroic absorbance of the methoxy-moieties ($\nu_{\mathrm{MeO}} = 1249\ \mathrm{cm}^{-1}$ [37]), with the strongest absorption being found when the azobenzene chromophores are positioned parallel to the IR analyzer, denoted here the “0°-position.” This behavior is in agreement with previous reports on **1** where it has been established that an ordered, “fork-like” molecular conformation is obtained through photo-alignment [33], with the side-groups of the trisazobenzene compound oriented perpendicular to the polarization direction of the

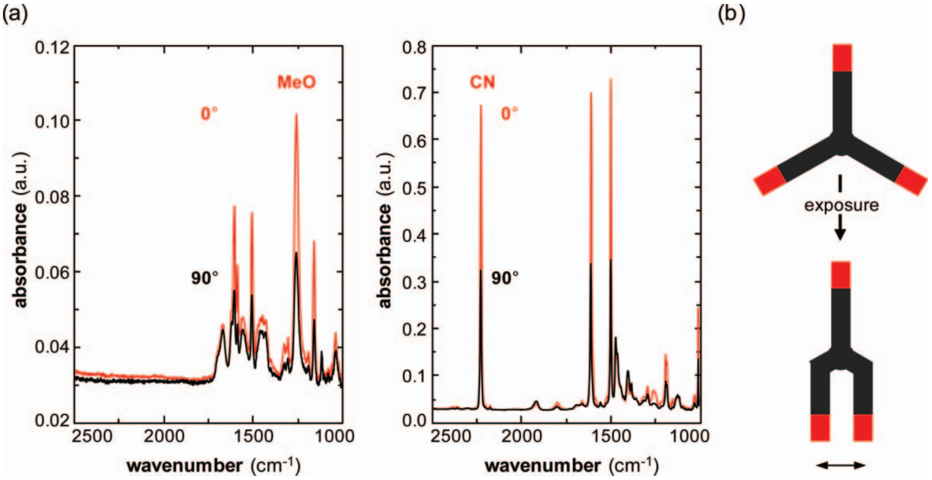

Figure 2. (a) Polarized infrared spectra of an empty cell constructed with trisazobenzene **1**-coated sodium chloride substrates, irradiated for 2 hours with linearly polarized light (left). Spectra of the same cell filled with 7CB (right). 0° denotes the direction parallel (90° perpendicular) to the azobenzene chromophores, which is perpendicular to the polarization of the light employed for photo-alignment. (b) Schematic illustration of the conformation of trisazobenzene **1** before (left) and after (right) exposure to linearly polarized light. Polarization direction indicated by double arrow.

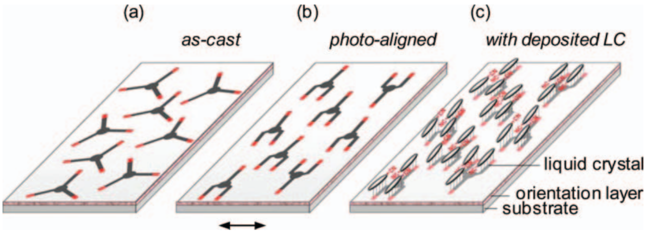

Figure 3. Cartoon of the molecular arrangement of trisazobenzene compound **1** in an as-cast layer (a); after photo-alignment of **1** (b); and with the liquid crystal compound applied (c). The direction of polarization of the inscribing light employed for the photo-alignment in (b) is indicated with the arrow.

inscribing light beam (see schematic in Fig. 2b). Thus, because of the configuration of the polarizer and the grating mask (see Fig. 1b), the illuminated regions of **1** were comprised of material with its azobenzene moieties oriented at an angle of ±45° vis-à-vis the linear grating.

Having established that the patterned photo-alignment also was successful in the cell architecture, subsequently, they were filled with **2**. The absorbance due to the LC materials' cyano-groups ($\nu_{\mathrm{CN}} = 2227\ \mathrm{cm}^{-1}$ [38]) was found to feature a similar anisotropy as that of the methoxy-groups in the trisazobenzene layer; i.e., the strongest absorption was recorded perpendicular to the polarization direction of the inscribing light used to photo-orient **1** (*cf.* Fig. 2a). We, therefore, conclude that the cyano-groups of the LC species are oriented along the side-groups of the trisazobenzene derivative, as schematically indicated in Fig. 3, which suggests that the orientation is induced via intermolecular attraction, i.e., "molecular epitaxial" effects.

The latter hypothesis is supported by SEM and AFM on trisazobenzene layers again irradiated through the grating mask. SEM and AFM images of both the virgin and exposed areas of these layers are presented in Figs 4(a) and (b), respectively. The latter appeared to

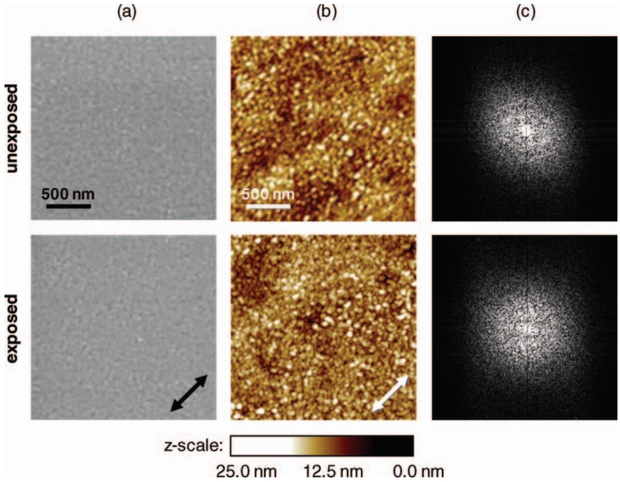

Figure 4. (a) SEM images, and (b) AFM images, and (c) Fourier transform AFM patterns of unexposed (top) and photo-oriented (bottom) areas of a trisazobenzene layer revealing the absence of any oriented surface relief structures; the alignment direction of the azobenzene chromophores is indicated with arrows.

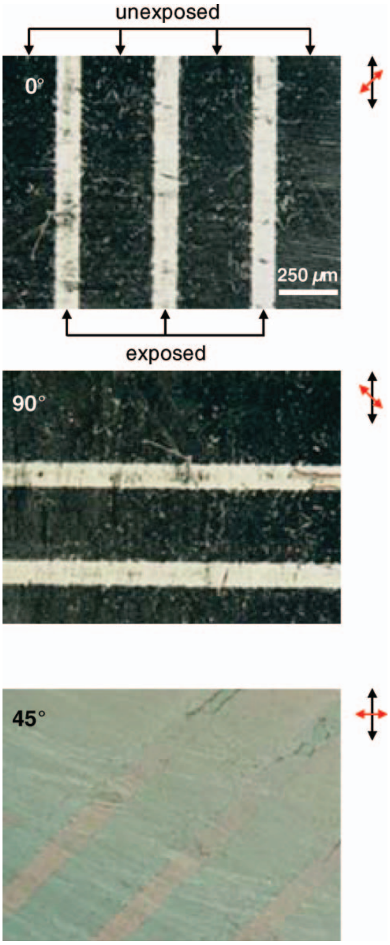

Figure 5. Polarized optical micrographs of an LC cell comprising patterned layers of **1**, filled with the nematic liquid crystal 7CB, revealing alignment of the LC in the exposed areas. The alignment of trisazobenzene in irradiated areas, which is in the direction perpendicular to the polarization direction of the light employed for photo-alignment, is indicated with red arrows, and the polarizer/analyzer positions in microscopy studies with black arrows.

be virtually identical in both cases and lacked any sign of ordered surface relief features at any length scale, from the 200 μm range to the nm-regime, that could have been responsible for the alignment of LC compounds, through a phenomenon generally referred to as mesoepitaxy [2]. Also, Fourier transforms of the AFM images revealed no features that indicate any preferred texture in the trisazobenzene surface induced by the exposure to polarized light (*cf.* Fig. 4c). The overall roughness of the film surface was determined to be of an average value, R_a, of less than ~2 nm, over the entire film.

The ease with which the trisazobenzene-based alignment layers are photo-aligned in well-defined areas, resulting in molecular orientation of **2** in these regions, can, of course, be exploited for optical patterning. This is illustrated by the optical micrographs presented in Fig. 5 of filled LC cells, taken with the linear grating produced with the shadow mask positioned at angles of, respectively, 0° and 90° with respect to the polarizer/analyzer position. The layer comprised of **2** is strongly birefringent only in the areas where the cell alignment layers had been exposed to polarized light, due to the molecular orientation that therefore is induced in this part of the structure. Care has, however, to be taken that no molecular orientation is induced in the liquid crystalline materials when filling the cell, that can result in weak birefringence in both exposed and unexposed areas, as is visible in the bottom optical micrograph in (Fig. 5).

4. Conclusions

We presented a simple method—employing photo-aligned trisazobenzene derivative films—to produce in-plane alignment substrates that can readily be patterned to create complex multi-domain architectures in a single step.

Acknowledgment

The authors are deeply indebted to Ivelina Shishmanova, Cees Bastiaansen, and Dick Broer (Technical University of Eindhoven, The Netherlands) for invaluable expert assistance with LC cell fabrication, as well as for numerous stimulating discussions. In addition, Karin Bernland and Kirill Feldman (ETH Zürich, Switzerland) are gratefully acknowledged for their support with SEM and AFM analysis.

References

[1] Mauguin, C. (1913). *C. R. Hebd. Séances Acad. Sci.*, *156*, 1246.
[2] Cognard, J. (1982). *Mol. Cryst. Liq. Cryst., Suppl.*, *1*, 1.
[3] Becker, M. E., Kilian, R. A., Kosmowski, B. B., & Mlynski, D. A. (1986). *Mol. Cryst. Liq. Cryst.*, *132*, 167.
[4] Geary, J. M., Goodby, J. W., Kmetz, A. R., & Patel, J. S. (1987). *J. Appl. Phys.*, *62*, 4100.
[5] Ishihara, S., Wakemoto, H., Nakazima, K., & Matsuo, Y. (1989). *Liq. Cryst.*, *4*, 669.
[6] van Aerle, N. A. J. M., Barmentlo, M., & Hollering, R. W. J. (1993). *J. Appl. Phys.*, *74*, 3111.
[7] Toney, M. F., Russell, T. P., Logan, J. A., Kikuchi, H., Sands, J. M., & Kumar, S. K. (1995). *Nature*, *374*, 709.
[8] Stöhr, J., Samant, M. G., Cossy-Favre, A., Diaz, J., Momoi, Y., Odahara, S., & Nagata, T. (1998). *Macromolecules*, *31*, 1942.
[9] Varghese, S., Crawford, G. P., Bastiaansen, C. W. M., de Boer, D. K. G., & Broer, D. J. (2004). *Appl. Phys. Lett.*, *85*, 230.
[10] Berreman, D. W. (1972). *Phys. Rev. Lett.*, *28*, 1683.
[11] Wolff, U., Greubel, W., & Krüger, H. (1973). *Mol. Cryst. Liq. Cryst.*, *23*, 187.
[12] Kawatak, Y., Takatoh, K., Hasegawa, M., & Sakamoto, M. (1994). *Liq. Cryst.*, *16*, 1027.
[13] Wittmann, J. C., & Smith, P. (1989). US Patent No. 5180470.
[14] Wittmann, J. C., & Smith, P. (1991). *Nature*, *352*, 414.
[15] Schadt, M., & Helfrich, W. (1971). *Appl. Phys. Lett.*, *18*, 127.
[16] Schadt, M. (1997). *Annu. Rev. Mater. Sci.*, *27*, 305.
[17] Broer, D. J., van Haaren, J. A. M. M., van de Witte, P., & Bastiaansen, C. (2000). *Macromol. Symp.*, *154*, 1.
[18] Kawamoto, H. (2002). *Proc. IEEE*, *90*, 460.
[19] Schadt, M., Schmitt, K., Kozinkov, K., & Chigrinov, V. (1992). *Jpn. J. Appl. Phys.*, *31*, 2155.
[20] Schadt, M., Seiberle, H., & Schuster, A. (1996). *Nature*, *381*, 212.
[21] Ichimura, K., Akita, Y., Akiyama, H., Kudo, K., & Hayashi, Y. (1997). *Macromolecules*, *30*, 903.
[22] Obi, M., Morino, S., & Ichimura, K. (1999). *Chem. Mater.*, *11*, 656.

[23] Lee, S. W., Kim, S. I., Lee, B., Choi, W., Chae, B., Kim, S. B., & Ree, M. (2003). *Macromolecules*, *36*, 6527.

[24] Ichimura, K., Suzuki, Y., Seki, T., Hosoki, A., & Aoki, K. (1988). *Langmuir*, *4*, 1214.

[25] Gibbons, W. M., Shannon, P. J., Sun, S.-T., & Swetlin, B. J. (1991). *Nature*, *351*, 49.

[26] Kosa, T., & Palffy-Muhoray, P. (1996). *Pure Appl. Opt.*, *5*, 595.

[27] Ichimura, K. (2000). *Chem. Rev.*, *100*, 1847.

[28] O'Neill, M., & Kelly, S. M. (2000). *J. Phys. D: Appl. Phys.*, *33*, R67.

[29] Schadt, M. (2001). *Mol. Cryst. Liq. Cryst.*, *364*, 151.

[30] Huang, D. D., Pozhidaev, E. P., Chigrinov, V. G., Cheung, H. L., Ho, Y. L., & Kwok, H. S. (2004). *Displays*, *25*, 21.

[31] Kwok, H.-S., Chigrinov, V. G., Takada, H., & Takatsu, H. (2005). *J. Display Technol.*, *1*, 41.

[32] Kreger, K., Wolfer, P., Audorff, H., Kador, L., Stingelin-Stutzmann, N., Smith, P., & Schmidt, H.-W. (2010). *J. Am. Chem. Soc.*, *132*, 509.

[33] Wolfer, P., Audorff, H., Kreger, K., Kador, L., Schmidt, H.-W., Stingelin, N., & Smith, P. (2011). *J. Mater. Chem.*, *21*, 4339.

[34] Gray, G. W., & McDonnell, D. G. (1979). *Mol. Cryst. Liq. Cryst.*, *53*, 147.

[35] Berreman, D. W., & Heffner, W. R. (1980). *Appl. Phys. Lett.*, *37*, 109.

[36] Oweimreen, G. A., & Morsy, M. A. (2000). *Thermochim. Acta*, *346*, 37.

[37] Lefevre, R. J. W., & Werner, R. L. (1957). *Aust. J. Chem.*, *10*, 26.

[38] Tsujimoto, A., & Goto, H. (2008). *Mol. Cryst. Liq. Cryst.*, *493*, 82.