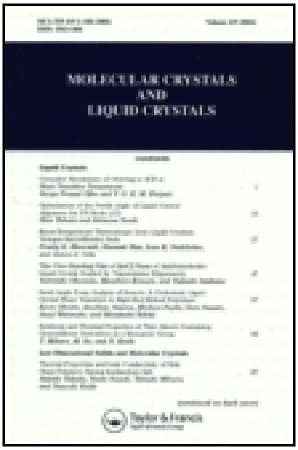


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Alignment Properties of Hydrogen-Bonded Mesogens of Supramolecular Liquid-Crystalline Network Films Coated on an Alignment Layer

Motohiro Yamahara [a], Masaya Moriyama [b c] & Takashi Kato [b]

[a] IT-Related Chemicals Research Laboratory, Sumitomo Chemical Co., Ltd., Osaka, Japan

[b] Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, Tokyo, Japan

[c] Deparment of Applied Chemistry, Faculty of Engineering, Oita University, Oita, Japan

Version of record first published: 05 Oct 2009

To cite this article: Motohiro Yamahara, Masaya Moriyama & Takashi Kato (2009): Alignment Properties of Hydrogen-Bonded Mesogens of Supramolecular Liquid-Crystalline Network Films Coated on an Alignment Layer, Molecular Crystals and Liquid Crystals, 510:1, 96/[1230]-105/[1239]

To link to this article: http://dx.doi.org/10.1080/15421400903058676

Mol. Cryst. Liq. Cryst., Vol. 510, pp. 96/[1230]–105/[1239], 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903058676

Alignment Properties of Hydrogen-Bonded Mesogens of Supramolecular Liquid-Crystalline Network Films Coated on an Alignment Layer

Motohiro Yamahara[1], Masaya Moriyama[2,3], and Takashi Kato[2]
[1]IT-Related Chemicals Research Laboratory, Sumitomo Chemical Co., Ltd., Osaka, Japan
[2]Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, Tokyo, Japan
[3]Deparment of Applied Chemistry, Faculty of Engineering, Oita University, Oita, Japan

*The films of a supramolecular liquid-crystalline (LC) network were spontaneously formed by intermolecular hydrogen bonds between multifunctional H-bond donor (HD) and H-bond acceptor (HA) molecules. A tricarboxylic acid, 2,5-bis{2-[2-(4-carboxyphenoxy)ethoxy]ethoxy}benzoic acid (***1***) was prepared for the use as a trifunctional H-bond donor. This donor was complexed with a bifunctional H-bond acceptor, trans-1,2-bis(4-pyridyl)ethylene (***2***). H-bonded complexes,* **1/2***, in the various ratio of donor to acceptor groups (HD/HA) were coated on a rubbed poly(vinyl alcohol) (PVA) film. These films exhibited homogeneous alignment when the ratio of HD to HA (HD/HA) was more than 1.025. These results suggest that the alignment properties of the mesogens in the complex films on the PVA film related to the value of HD/HA.*

Keywords: alignment film; hydrogen-bonded mesogen; inclination angle; molecular orientation; rubbing treatment; supramolecular liquid crystal

1. INTRODUCTION

Thin films comprised of oriented molecules are used for optical retardation films in liquid crystal displays, organic semiconductor

---

The authors would like to thank Song Qui, Dr. Hikaru Hasegawa, Michiko Yamanaka and Tadahiro Kobayashi, for technical assistance.

Address correspondence to Motohiro Yamahara, IT-Related Chemicals Research Laboratory, Sumitomo Chemical Co., Ltd., 1-98 Kasugadenaka 3-chome, Konohana-ku, Osaka 554-8558, Japan. E-mail: yamaharam@sc.sumitomo-chem.co.jp

materials, etc. It is expected that the improvement in functional and new characteristics will be found by ordering molecules. Almost all those films are provided by coating on a substrate. As an immobilization method of the molecular orientation, the photopolymerization of the liquid-crystalline (LC) monomers is generally used. These photopolymerized LC films have been reported from 1989 [1–3]. In the fabrication process of these films, the LC monomer solutions are usually applied on alignment layers of the rubbed organic membranes such as polyimide (PI) and poly(vinyl alcohol) (PVA), etc. After drying, the LC monomers are aligned in one direction and are subsequently photopolymerized by UV irradiation. However, in this process it is necessary to add impurities such as a polymerization initiator and a leveling agent in this liquid crystal monomer solution. This means that the factors which check the orientation of LC molecules are added. It was reported after the photopolymerization process the mesogen ordering of the photopolymerized LC film slightly decreased [4,5]. In the photopolymerization process, the conditions such as the UV dose, the UV intensity, and the irradiation time must be tuned. These conditions affect the mesogen orientation of the photopolymerized LC films. Since the orientation degree of the LC monomers is decreased by the photopolymerization process, the potential function may not fully be pulled out. Then, it is necessary to adopt a new immobilization technology of the molecular orientation which does not use the photopolymerization process.

As new technology, we are interested in a molecular self-assembly process through hydrogen bonding. Kato *et al.* have already reported that supramolecular liquid-crystalline complexes which show a variety of mesophases can be prepared through intermolecular H-bonding [6–8]. They also prepared liquid-crystalline H-bonded networks by the self-assembly process involving multifunctional H-bonding donor and acceptor molecules [7]. Moreover, nematic glassy phases were observed for some these complexes [7].

In this study, the alignment behavior of H-bonded mesogens of supramolecular LC network films on the rubbed PVA film was examined using optical measurements. Our aim was to make one-directionally aligned LC domains of these complexes on this alignment layer. These supramolecular LC network films were spontaneously formed by intermolecular H-bonds between multifunctional H-bond donor and acceptor molecules. Transmission spectro-ellipsometry was applied to characterize the optical properties of the films. The optical properties of the H-bonded complex films under various ratio of H-bond donor to acceptor groups (HD/HA) were measured, and the influence of the HD/HA upon the mesogen orientations of H-bonded networks on the alignment layer is discussed.

2. EXPERIMENTAL

The fabrication process coating the H-bonded complex film is shown in Figure 1. All samples were prepared on 1737 glass substrates (Corning). The PVA material POVAL PVA-HC (KURARAY Co., Ltd., Japan) was spin-coated on the glass substrates. The PVA-coated glass was heated to 80°C for 5 min, and then baked at 100°C for 60 min. The PVA layer was subsequently rubbed using a velvet cloth (Yoshikawa-Chemical, Japan, YA-20-RW) in an LQ-008-kai rubbing machine (JOYO ENGINEERING CO., LTD. Japan). The standard rubbing conditions were as follows: rotation speed $f = 450$ rpm, push length $l = 0.3$ mm, transfer speed $V = 12$ mm/s and cumulative number of rubs $N = 1$.

A tricarboxylic acid, 2,5-bis{2-[2-(4-carboxyphenoxy)ethoxy]ethoxy benzoic acid (**1**) was prepared for the use as a trifunctional H-bond donor. This trifunctional H-bond donor was complexed with a bifunctional H-bond acceptor, *trans*-1,2-bis(4-pyridyl)ethylene (**2**) (TOKYO CHEMICAL INDUSTRY CO., LTD., Japan), maintaining a 1:1 donor/acceptor group stoichiometry. The structures of these H-bond donor and acceptor compounds are shown in Figure 2. The compounds **1** and **2** were dissolved in *N*,*N*-dimethylacetamide (DMAc) in the concentration of 30 wt%, and the solutions in the various ratio of donor and acceptor groups (HD/HA) were prepared. The solutions of **1**/**2** were spin-coated on a rubbed PVA film. In order to align the supramolecular

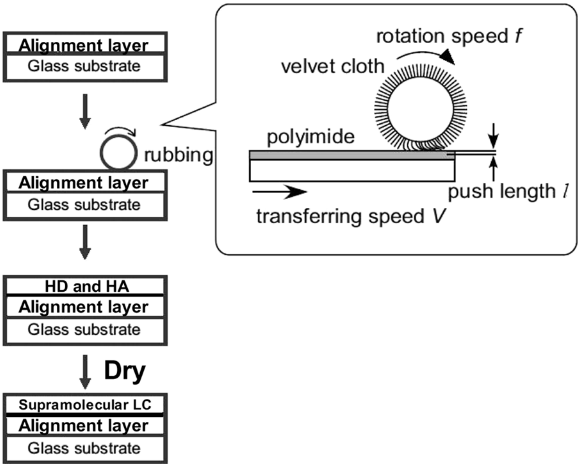
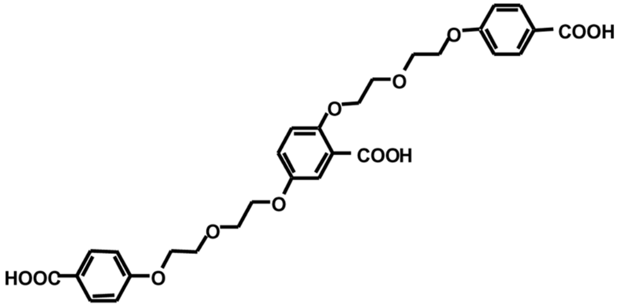
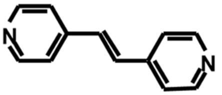


FIGURE 1 Fabrication of one-dimensionally aligned self-assembly H-bonded LC network films.



(1) Trifunctional H-bond donor



(2) Bifunctional H-bond acceptor

FIGURE 2 Structures of compounds used in this study.

LC network, the H-bonded complex film was heated at 55°C for 5 min. The textures of these H-bonded complex films were observed using a BX51 polarizing microscope (OLYMPUS) equipped with a 10039 L hot stage (JAPAN HIGH TECH CO., LTD.). The polar angle dependence of the H-bonded complex films was measured with a KOBRA-WR automatic birefringence analyzer (Oji Scientific Instruments, Japan). The inclination angle of the refractive index ellipsoid of the H-bonded complex films (β) was measured according to previous studies [9,10]. The definition of the inclination angle β is shown in Figure 3.

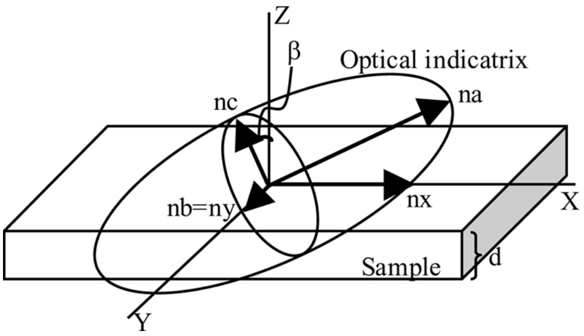


FIGURE 3 Refractive index ellipsoid of the samples.

Thicknesses of the films were measured by a LEXT OLS3000 confocal scanning microscope (OLYMPUS). The thickness of the PVA alignment layer was 0.12 μm and that of the H-bonded LC complex films was 0.29 μm.

3. RESULTS AND DISCUSSION

3.1. One-Directionally Aligned H-Bonded Mesogens of the LC Network Film

The structures of the multifunctional H-bonding molecules used in the present study are shown in Figure 2. Compound **1** is a benzoic acid with two benzoic acid moieties as substituents in its 2 and 5 positions. Bipyridyl molecule **2** was used as the bifunctional H-bonding acceptor molecule. Compound **2** was previously reported to form low molecular weight supramolecular 1:2 mesogenic complexes with 4-alkoxybenzoic acids [11,12]. In this case, the bipyridine functions as a part of the central core unit of the H-bonded mesogen. Compounds **1** and **2** are nonmesogenic and their melting temperatures are 127 and 152°C, respectively [7,8].

The H-bonded complex **1**/**2** was prepared from the trifunctional H-bonding donors and the bifunctional H-bonding acceptors, maintaining the 1:1 stoichiometry of carboxylic acid and pyridine moieties. It was expected that intermolecular mesogenic structures were formed by complexation of these molecules. The phase of this H-bonded complex **1**/**2** was determined by DSC measurement. DSC measurements were performed with a DSC30 (METTLER) at a scanning rate of 10C°/min on heating and cooling. The DSC thermogram of complex **1**/**2** is shown in Figure 4. The temperature range of the nematic phase was 150–156°C on heating. The temperatures of the isotropic-nematic and the glass transitions on cooling were 154 and 35°C, respectively. A polarized optical photomicrograph of the complex **1**/**2** at 26°C is shown in Figure 5. The schlieren texture is maintained for a glassy sample of complex **1**/**2** at 26°C on cooling, however, fluidity is no longer observed at this temperature. This result suggests that the H-bonded complex **1**/**2** formed the nematic glassy state.

The formation of the one-directionally aligned LC domain for this complex **1**/**2** was examined. The solution of the H-bond donor and acceptor molecules in DMAc was spin-coated on the rubbed surface of the PVA film and then dried. The liquid-crystalline H-bonded networks were obtained on the alignment layer by a self-assembly process. Figure 6 shows polarized optical photomicrographs of complex

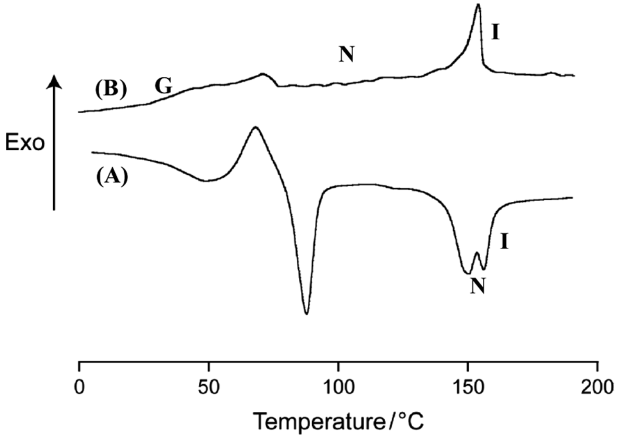


FIGURE 4 DSC thermograms of H-bonded complex **1**/**2** on (A) heating scan and (B) cooling scan.

1/**2** on the rubbed PVA film at 26°C. This H-bonded complex film has optical anisotropy, and fluidity is no longer observed at this temperature. This texture of aligned nematic glassy state was kept until 150°C on heating. These results suggest that H-bonded mesogens of this complex on the alignment layer form one-directionally aligned LC domain and their orientation is fixed below 150°C.

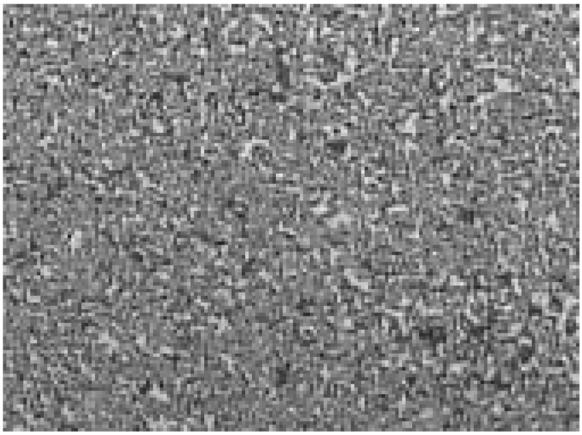


FIGURE 5 A photomicrograph of nematic glassy state of **1**/**2** at 26°C on cooling.

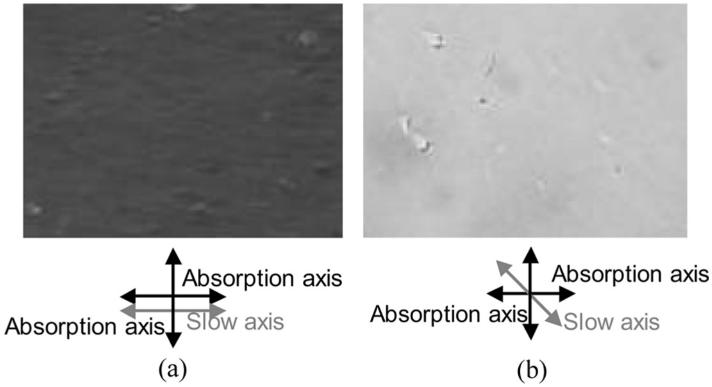


FIGURE 6 Photomicrographs of nematic glassy state of the **1**/**2** complex film at 26°C: (a) The slow axis is parallel to the absorption axis, (b) The slow axis is not parallel to the absorption axis.

3.2. Influence of the HD/HA upon the Mesogen Orientations of H-Bonded Networks on the Alignment Layer

The influence of the HD/HA ratio upon the orientation of H-bonded mesogens of the LC network films on a rubbed PVA alignment layer was investigated. The HD/HA ratio was varied from 0.80 to 1.10. Figure 7 shows polar angle dependence of retardation for the H-bonded complex film in HD/HA = 0.975. The optical properties

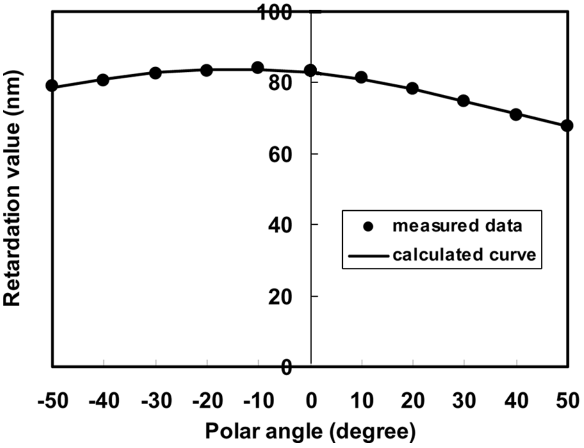


FIGURE 7 Polar angle dependence of retardation for the H-bonded complex film and calculated curve of refractive index ellipsoid.

of this film are dominated by the molecular orientation of H-bonded mesogens. The retardation value (Re) is defined as the difference in the optical path lengths between an ordinary and an extraordinary ray:

$$Re = d\Delta n \tag{1}$$

where d is the film thickness and Δn is the optical anisotropy ($\Delta n = na - nb$, Fig. 3). The optical anisotropy, Δn, arises from ordering of molecules in a film. The inclination angel of the refractive index ellipsoid, β, shows the tilt angle of the ordering H-bonded mesogens in the LC network films. The measurement data points and the fitting calculated curve from refractive index ellipsoid were plotted in Figure 7 according to previous studies [9,10]. The optical characteristics of the LC network films can be obtained by transmission ellipsometry technology. We set the inclination direction of the refractive index ellipsoid shown in Figure 3 to be perpendicular to the rotation axis of the films (nb). Then, retardation values with respect to the polar angle were measured. The polar angle is equivalent to the angle of the incident light and the viewing angle. The curves are simulated using the equations of the ideal refractive index ellipsoid [9,10]. Based on these equations, we did a curve fit of the retardation values versus the polar angel of the biaxial refractive index ellipsoid that most closely approximated the measured data. We were able to estimate the principal indices of refraction (na, nb, nc), as well as the inclination angle (β). When this retardation versus polar angle curve deviates from the curve for measured data, it means that no model for the refractive index ellipsoid is defined for the H-bonded complex film. Figure 7 shows that the calculated result is in good agreement with this measured data. This implies that the optical properties of the H-bonded complex film on the rubbed PVA film are treated as an inclined biaxial refractive index ellipsoid. The inclination angle (β) and the optical anisotropy (Δn) of the H-bonded complex film were measured to be 4.34° and 0.272, respectively. These results suggest that the refractive index ellipsoid of this H-bonded LC network film is inclined uniaxial positive birefringence.

The optical anisotropy (Δn) and the inclination angle (β) of the H-bonded complex films on alignment layer are plotted as a function of the HD/HA ratio in Figure 8. As seen in Figure 8(a), Δn slightly changes with increasing the HD/HA ratio. However, in this change order, the orientation of the H-bonded mesogens of the LC network films is maintained. Thus, the degree of the orientation of the H-bonded mesogens is not influenced by the HD/HA ratio. As seen

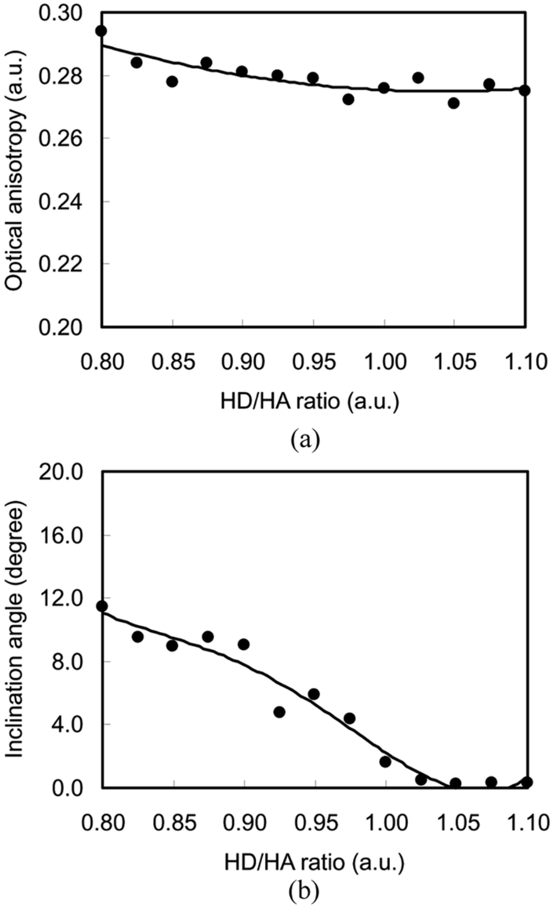


FIGURE 8 Influence of the HD/HA ratio on the optical properties of the H-bonded complex **1**/**2** on the rubbed PVA film: (a), optical anisotropy (Δn); and (b), inclination angle (β).

in Figure 8(b), the inclination angle of the H-bonded complex film (β) decreased with the HD/HA ratio up to 1.025. The tilt angel of the H-bonded mesogens is influenced by the HD/HA ratio. Thus, these results indicate that the tilt angles of the H-bonded mesogens are tuned while maintaining these ordering mesogens with the HD/HA ratio. As the amount of H-bonded acceptor is excessive for these H-bonded complex films, pyridine rings free of H-bonding exist at the periphery of the supramolecular LC networks. When the HD/HA HA ratio is 1.025 and over, the inclination angles of the H-bonded complex film on the rubbed PVA film (β) are 0°. This result shows that the H-bonded complex films have homogeneous alignment with HD/HA $\geq$ 1.025. In this case, free carboxyl groups may exist at the periphery of the LC networks because the H-bond donor is excessive. Thus, the tilt angels of the H-bonded mesogens were controlled by varying the HD/HA ratio, which changes the interaction modes of the complexes with the surface, while maintaining the degree of molecular orientation of the H-bonded complex films.

4. CONCLUSIONS

The molecular orientation of the films prepared by supramolecular LC networks has been studied. The supramolecular LC network films were spontaneously formed by intermolecular H-bonds between H-bond donor and acceptor molecules on the rubbed PVA film. The mesogens of these complex films had one-directionally aligned LC domains. The alignment properties of the mesogens in the H-bonded complex films on the alignment layer depend on the HD/HA ratio. The tilt angles of these H-bonded mesogens can be tuned while maintaining the mesogen orientation. It was found that as long as the HD/HA ratio values are 1.025 and over, these H-bonded complex films have homogeneous alignment.

REFERENCES

[1] Broer, D. J., Boven, J., Mol, G. N., & Challa, G. (1989). *Makromol Chem.*, *190*, 2255.
[2] Broer, D. J., Gossink, R. G., & Hikmet, R. A. M. (1990). *Angew. Makromol. Chem.*, *183*, 45.
[3] Mori, H., Itoh, Y., Nakamura, T., & Shinagawa, Y. (1997). *Jpn. J. Appl. Phys.*, *36*, 143.
[4] Yamahara, M., Nakamura, M., Koide, N., & Sasaki, T. (2007). *Liq. Cryst.*, *34*, 381.
[5] Yamahara, M., Nakamura, M., Koide, N., & Sasaki, T. (2007). *Mol. Cryst. Liq. Cryst.*, *473*, 3.
[6] Kato, T. & Fréchet, J. M. J. (1995). *Mcromol. Symp.*, *98*, 311.
[7] Kato, T., Kihara, H., Uryu, T., & Fréchet, J. M. J. (1996). *Chem. Mater.*, *8*, 961.
[8] Kato, T., Kihara, H., Uryu, T., & Fréchet, J. M. J. (1998). *Liq. Cryst.*, *24*, 413.
[9] Yamahara, M., Inoue, I., Nakai, T., Yamada, Y., & Ishii, Y. (2002). *Jpn. J. Appl. Phys.*, *41*, 6027.
[10] Yamahara, M., Inoue, I., Nakai, T., & Mizushima, S. (2003). *Sharp Technical Journal*, *85*, 19.
[11] Kato, T., Fréchet, J. M. J., Wilson, P. G., Saito, T., Uryu, T., Fujishima, A., Jin, A., & Kaneuchi, F. (1993). *Chem. Mater.*, *5*, 1094.
[12] Kato, T., Uryu, T., Fujishima, A., & Fréchet, J. M. J. (1990). *Chem. Lett.*, 2003.