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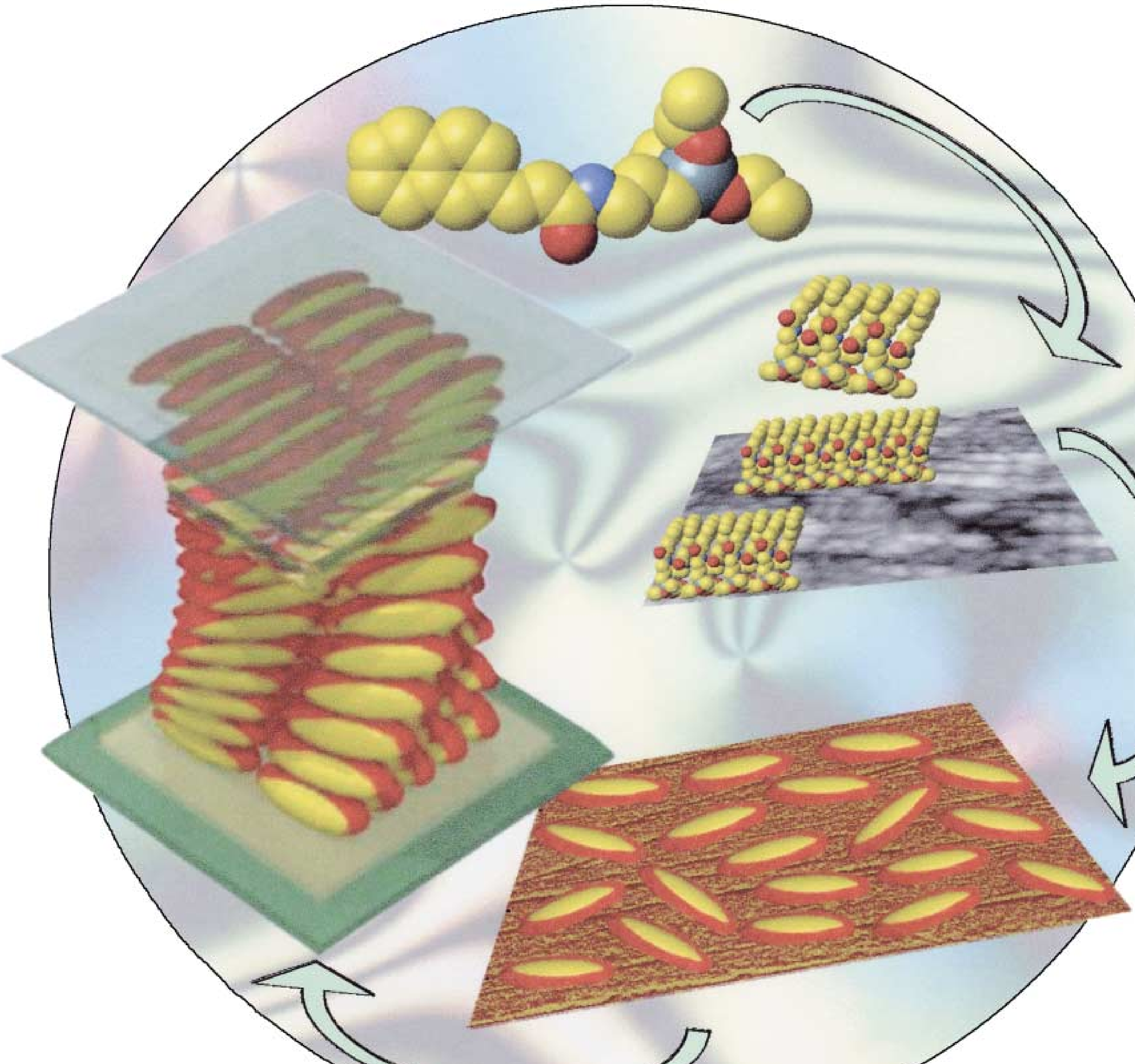

Hier dargestellt ist der Aufbau einer kontaktlosen Schicht für Flüssigkristalldisplays. Supramolekulare Wechselwirkungen liegen einem hierarchischen Prozess zur Bildung von starren Oligomeren in Lösung zugrunde, die an richtungsorientierende Keimbildungszentren auf einer ITO-Oberfläche knüpfen. Die entstehende gefurchte Oberfläche sowie deren Eigenschaften und Verwendungsmöglichkeiten beschreiben R. J. M. Nolte et al. auf den folgenden Seiten…

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Liquid-Crystal Alignment

Noncontact Liquid-Crystal Alignment by Supramolecular Amplification of Nanogrooves[**]

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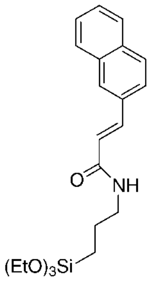
The construction of surfaces that control the orientation of liquid crystals (LCs) is of key importance in liquid-crystal display (LCD) technology. Current industrial manufacture of such surfaces involves the mechanical rubbing of polymers, which have been spin-coated onto an indium-tin oxide (ITO) surface, with a velvet cloth. This creates microscopic grooves on the surface, which form an alignment layer that causes the LCs to align in the direction of rubbing.[1] The invasive nature of this process causes the surface to be prone to the generation of electrostatic charges and to contamination from, for example, dust particles, which can lead to faulty pixels in the final product. Therefore, the development of less contact-intensive techniques to achieve LC alignment is a prerequisite for the production of cheap, large LCD screens.[2] In this report, we describe a very simple, robust, and completely non-contact method for creating an alignment layer, which eliminates the need for clean rooms, and is based on a hierarchical process involving supramolecular interactions and surface grafting that results in a more than 1000-fold amplification of the initial ITO surface ordering.

One widely investigated alternative to mechanical rubbing is photoinduced alignment, in which a cinnamic acid derivative is deposited onto a surface and irradiated with linearly polarized (UV) light.[2b,3] Although this procedure induces enough surface ordering for LC alignment, in most cases there is little control over the orientation of the photoswitches on the surface and the interaction with the LC is poor, compared to conventionally manufactured alignment layers. To have more control over the surface orientation, we designed and synthesized compound **1** , which can be covalently linked to the ITO surface. It contains a photoswitch with a large aromatic surface and an amide group, both of which can be expected to increase intermolecular interaction by π stacking and hydrogen bonding, possibly resulting in a surface which is better preorganized for LC alignment.



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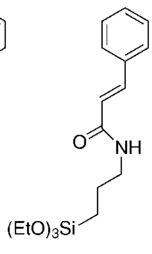

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A twisted nematic LCD (TN-LCD) was constructed by using one plate covered with **1** (from immersion in a 2 wt% toluene solution), without any conventional treatment to form an alignment layer (for example, irradiation with UV light or rubbing), and a conventionally rubbed polyimide (PI) counterplate (Figure 1 a). To our surprise, optical microscopy showed that about 80% of this cell was capable of liquid-crystal alignment. Scanning electron microscopy (SEM) and tapping-mode atomic force microscopy (TM-AFM) studies on the plates containing **1** revealed that the surface contained large domains of groove-like structures, which resemble those present in conventionally rubbed polymer alignment layers.[1b] The inherent ITO topography can alone serve as a template on which the grooves develop (see below). The grooves were 0.5–8.0 nm deep and hundreds of micrometers long (Figure 2 a and c). TM-AFM also showed that the width of the grooves are mainly found in two sizes; the largest have a width of 150–200 nm, while the smallest have an average width of 50 nm, the latter being the most predominant. The direction of the grooves could not be attributed to any dipping effect or flow effect; they were found to be independent even of intentionally induced flow or dipping. Furthermore, the grooves were not formed during the baking process (for example, by film cracking), as on unbaked plates the same structures were also formed.

The azimuthal anchoring energy (W_ϕ), which is an indication of the interaction energy between the alignment layer and the LC, was measured to be $1.8\times10^{-5}\,\mathrm{J\,m^{-2}}$ by using the cell-rotation method.[1b] This value is of the same order of magnitude as found for conventionally rubbed polymer alignment layers[1b] and about 20 times higher than observed for cinnamic acid-based systems in the literature,[2b,3a–3c,4] which suggests that increasing the π-electronic character of the molecules in the alignment layer improves the interaction with the LC molecules. Furthermore, attempts to change the alignment direction induced by the surface by irradiating the photoswitches with (polarized) light did not succeed, which is an indication that the LC-alignment capability of the surface is quite strong.

To investigate the origin of the formation of the alignment layer in more detail, a series of experiments was carried out. Ellipsometry measurements showed that the surface features

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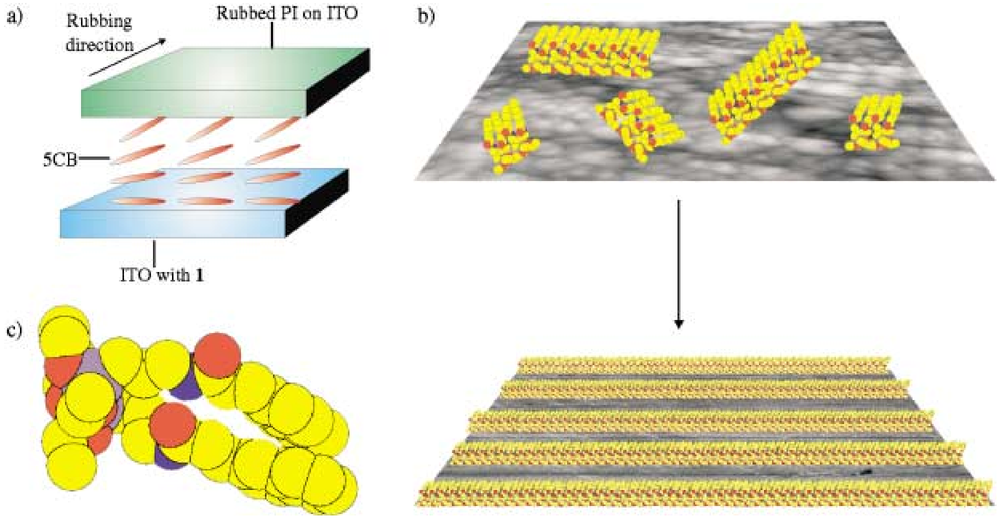

Figure 1. a) Schematic drawing of a twisted nematic LCD; 4-*n*-pentyl-4′-cyanobiphenyl (5CB) was used as the LC; b) proposed alignment of covalently linked oligomers of **1** on the surface of ITO resulting in a more than 1000-fold amplification of the initial ordering; c) lowest-energy structure (PM3) of the dimer of **1**.

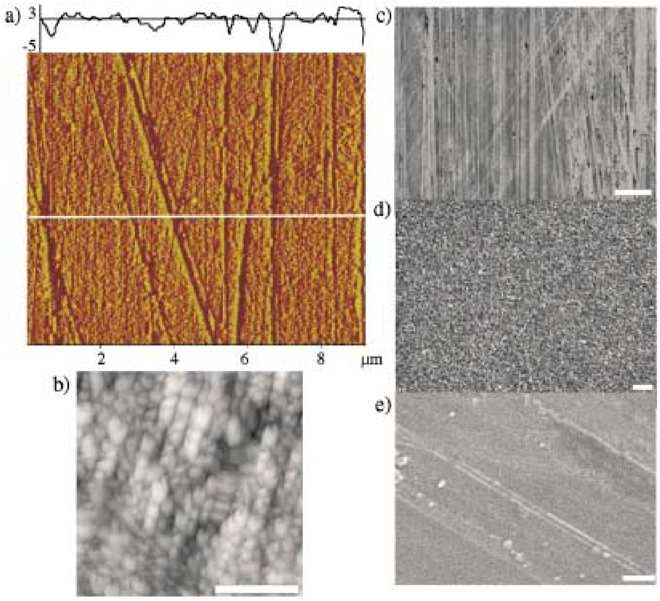

Figure 2. a) TM-AFM image of an ITO plate covered with **1**, above: the height profile along the displayed white line (nm); b) STM image of a blank ITO surface (bar = 100 nm); SEM images of ITO plates covered with: c) **1** from a 2 wt% solution at room temperature (bar = 10 µm); d) **2** from a 2 wt% solution at room temperature (bar = 1 µm); e) **1** from a 2 wt% solution at 90 °C (bar = 1 µm).

were formed within 6 min of the immersion of the plates into a monomer solution. From the ellipsometry data, a layer thickness of 8.0 ± 2.0 nm was calculated, which is in excellent agreement with the TM-AFM results. Since the length of a fully elongated molecule of **1** is only 1.6 nm, it can be assumed that the surface is partly covered by multilayers of **1**.

To determine the role π–π interactions and hydrogen bonding play in the formation of the alignment layer, reference compound **2** was synthesized. Although its crystal structure clearly showed the presence of a hydrogen-bonded array (Figure 3),[5] with the aromatic groups preorganized for LC alignment, ITO plates covered with **2** did not exhibit any grooves (Figure 2d), nor did they show LC-alignment capability. To explain this remarkable difference to **1**, we studied molecular recognition interactions for both molecules, in particular their self-association in solution and hydrogen-bond strength. Although the interactions are weak at the concentrations studied (0.2–20 wt% in toluene), it was clear that compound **1** formed stronger intermolecular hydrogen bonds than **2**. For instance, in 2 wt% solutions, the NH signals for **1** and **2** in their ^{1}H NMR spectra appeared at a $\delta = 5.45$ and 4.91 ppm, respectively. This difference was retained in the solid state, as highlighted by the frequency shifts between the

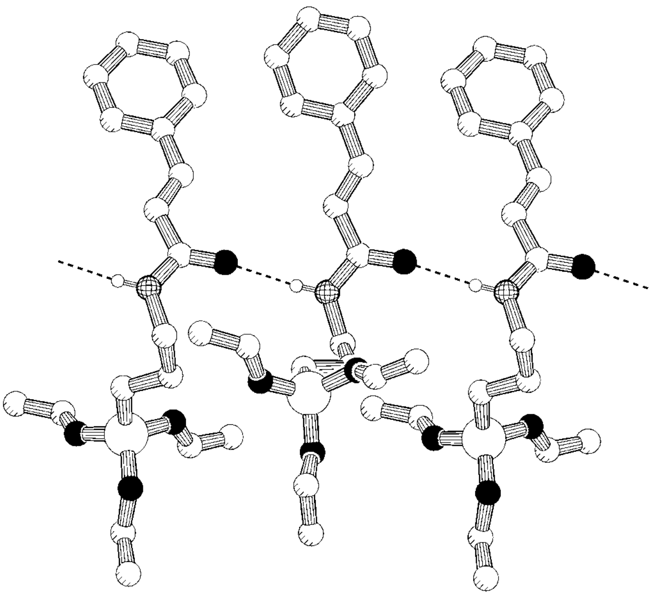

Figure 3. Representation of the unit cell of **2**, as determined by X-ray diffraction. Hydrogen atoms, except amide protons, are omitted for clarity. Hydrogen bonds are indicated by a dotted line.

two amide stretching vibrations ($\Delta\tilde{\nu}$) in their IR spectra, which were 97 and 105 cm^{-1} for **1** and **2**, respectively. Although we were not able to obtain crystals of **1** that were suitable for X-ray diffraction, the NMR and IR measurements suggest that hydrogen bonding occurs in the same geometry as between the molecules of **2**.

In solutions of **1** in toluene, covalently linked oligomers were shown to precipitate. Of these oligomers, only the dimer could be studied in solution; higher oligomers could not be redissolved. In a concentration range of 1–10 wt% in toluene, no oligomerization was observed for **2**. The dimer of **1** appeared to have a very strong intramolecular hydrogen bond; ^{1}H NMR spectroscopy showed an amide signal in THF at $\delta = 7.02$ ppm. In addition, 2D-NOESY measurements indicated that the dimer has a very well defined preferential geometry (Figure 1c). Solid-state IR spectroscopy displayed a very sharp NH stretching vibration at 3304 cm^{-1}, which indicates that the direction of the intramolecular hydrogen bond in the dimer is very well defined. With MALDI-TOF spectrometry, linear oligomers up to a heptamer and cyclic oligomers up to a decamer were observed. Solid-state IR spectroscopy showed two sharp NH stretching vibrations at 3421 and 3286 cm^{-1} for the mixture of oligomers, which also indicates strong, well defined, directional hydrogen bonding. The above data indicates that intramolecular hydrogen bonding is required for forming structurally well-defined oligomers.[6]

To investigate the role of the surface in the formation of the grooves, **1** was deposited onto isotropic quartz from 1–5 wt% solutions in toluene. The resulting surfaces displayed no grooves and did not show LC alignment, an indication that the ITO surface fulfils a crucial role in the formation of the alignment layer. Furthermore, scanning tunneling microscopy (STM) showed that the blank ITO surfaces used in these experiments intrinsically contain alignment seeds, so-called "nanogrooves". These ordered regions have dimensions of approximately 100 × 100 nm, are all aligned parallel to each other (see below), and are surrounded by isotropic ITO (Figure 2b). It is known that the morphology of the blank ITO surface can be strongly dependent on deposition conditions (for example, pressure, temperature, and ITO composition), and the occurrence of similar structures has been observed before.[7] To determine whether the surface controls the groove direction, an ITO plate was cut in half and the pieces were positioned at 90° with respect to each other in a 2 wt% solution of **1**. After the formation of the alignment layer, the direction of the grooves was found to be dependent on the initial rotation of the ITO plate in the solution, which shows that the underlying ITO dictates their general direction. Apparently, the chemisorption of **1** on to the ITO plate causes the small degree of surface-ordering to be amplified more than a thousand times.

The combined experimental results suggest that the deposition of structurally well-defined linear and cyclic oligomers of **1** amplifies the small groove-like surface features which are initially present on the ITO surface, and results in the formation of long parallel grooves (Figure 1b). Under layer-forming conditions, there are two (competing) processes: oligomerization in solution and surface grafting. Although the rate of the grafting reaction is not easily altered, the oligomerization can be influenced by changing the reaction conditions. When the concentration of **1** was lowered to 1 wt% or increased to 4 or 5 wt%, which respectively slows down and increases the oligomerization rate, the surface contained no discernable features. An increase in temperature to 90 °C, which accelerates the oligomerization reaction, resulted in a surface with approximately 85% less grooves (Figure 2e). None of these samples were capable of LC alignment. In the latter case, this is probably a result of the fact that the distance between the grooves is larger than the correlation length of the LC.[8] These experiments indicate that the fine balance between the rate of grafting and the formation of oligomers is a key factor in the formation of the grooves, which, in turn, is essential for successful LC alignment.

In summary, we have presented an easy and robust, noncontact procedure for constructing an alignment layer for LC alignment, based on a hierarchical process involving a combination of supramolecular interactions and surface grafting. The initial surface-ordering is amplified over a thousand times, going from small 100 nm-sized parallel domains already present on the underlying ITO surface, to spontaneously formed 100-μm long, aligned grooves that resemble those observed for conventionally rubbed polymer alignment layers. The present system displays an anchoring energy which is 20 times higher than that measured for comparable systems in the literature, and is in the same order of magnitude as observed for conventionally rubbed polymer alignment layers. Present research is focused on the effect of larger aromatic head groups on the surface morphology, and their influence on the LC alignment.

Experimental Section

TN-LCD cells with a thickness of 6 μm (Mylar spacer) were prepared according to the literature.[1b] The ITO used in these experiments was purchased from the Applied Film Corporation (6797 Winchester Circle, Boulder, CO 80301, USA); the exact manufacturing process is unknown to the authors. Ellipsometry measurements indicated that the ITO plates consisted of 20-nm thick ITO layer, coated by rf sputtering, over a polycrystalline SiO_2 layer (20 nm) on a 1.1-mm soda lime glass substrate (BK7). The ITO layer was polished by the manufacturer to obtain optical quality for LCD application. Sample plates were prepared by immersing an ozone-cleaned ITO or quartz plate in a solution of **1** or **2** in toluene, with a drop of acetic acid which serves to activate the surface. After one hour, the plates were washed with dry acetonitrile and baked at 120 °C for 10 min. The PI counterplate was prepared by spin-coating with a 2 wt% solution of Pyralin PI2555 (HD Microsystems) in 1-methyl-2-pyrrolidinone, after which it was baked at 180 °C for 60 min. The plate was rubbed with a home-built rubbing machine. LP-UV irradiation was achieved with a 150 W Xe lamp, $180 < \lambda < 350$ nm, at an intensity of 0.15 mW cm^{-2} for 20 min. The cells were filled with 4-*n*-pentyl-4′-cyanobiphenyl (5CB; $T_{NI} = 35.3$ °C), heated to 40 °C, and then cooled to room temperature. In all experiments, at least five plates were examined. Seven working TN-cells were made of ITO with **1** and rubbed PI.

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Keywords: hydrogen bonds · liquid crystals · pi interactions · self-assembly · supramolecular chemistry

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[5] X-ray crystal data for **2** at 293 K ($C_{18}H_{29}NO_4Si$, $M_r = 351.51$): monoclinic, space group $P2_1/a$, $\rho_{calcd} = 1.143\ \text{g cm}^{-3}$, $Z = 4$, $a = 9.7056(10)$, $b = 17.8378(17)$, $c = 12.599(2)$ Å, $\beta = 110.578(16)°$, $V = 2042.0(4)$ Å^3. Enraf-Nonius CAD4 diffractometer, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å. A single crystal with linear dimensions of 0.40 × 0.33 × 0.22 mm was grown from a hexane solution at 295 K. A semi-empirical absorption correction, based on ψ scans, was applied to the data ($T_{max} = 1.051$, $T_{min} = 0.928$). The structure was solved by Patterson and direct methods (DIRDIF-96) and refined by full-matrix least-squares (SHELXL-97), using $w = 1/[\sigma^2(F_o^2) + (0.0987P)^2 + 2.0737P]$, where $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. H-atom positions are based on stereochemical considerations. Final $R(F) = 0.0904$, $wR(F^2) = 0.2081$ for 217 parameters and 1235 reflections with $I > 2\sigma(I)$ and $2.86 < \theta < 22.98°$ (corresponding R values based on all 3021 reflections are 0.2036 and 0.2662, respectively). CCDC-192583 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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