Length Scale Selects Directionality of Droplets on Vibrating Pillar Ratchet

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Directional control of droplet motion at room temperature is of interest for applications such as microfluidic devices, self-cleaning coatings, and directional adhesives. Here, arrays of tilted pillars ranging in height from the nanoscale to the microscale are used as structural ratchets to directionally transport water at room temperature. Water droplets deposited onto vibrating chips with a nanostructured ratchet move preferentially in the direction of the feature tilt while the opposite directionality is observed in the case of microstructured ratchets. This remarkable switch in directionality is consistent with changes in the contact angle hysteresis. To glean further insights into the length scale dependent asymmetric contact angle hysteresis, the contact lines formed by a nonvolatile room temperature ionic liquid placed onto the tilted pillar arrays were visualized and analyzed in situ in a scanning electron microscope. The ability to tune droplet directionality by merely changing the length scale of surface features all etched at the same tilt angle would be a versatile tool for manipulating multiphase flows and for selecting droplet directionality in other lap-on-chip applications.

1. Introduction

Controlling droplet motion is of significant interest for a broad range of applications including microfluidics,[1,2] water harvesting,[3,4] printing,[5] and chemical sensing.[6] The use of asymmetrically structured surfaces, commonly referred to as ratchets, has been widely investigated as a means to control multiphase fluid flows, in particular droplet motion. The ideas of designing and using asymmetric micro- or nanostructures are often mimics of biological objects, such as the hierarchical scales on butterfly wings,[6,7] hierarchical hairs on a gecko foot,[8] knots on spider silk,[9] or capillaries on roach legs.[4] These biological inspired systems enable droplet motion via capillary phenomena,[10–12] mechanical vibrations,[13] chemical patterning,[14–16] and gradients of texture.[17,18] In addition, deterministically designed systems provide a robust, manufacturable platform that can even take advantage of unique scenarios not found in nature, such as the Leidenfrost effect[19] or reversible electrowetting.[20]

The ability for a hydrophobic structured ratchet surface to directionally transport droplets is typically determined by the contact angle hysteresis (CAH), where the value of CAH is the difference between the advancing contact angle (θadv) and the receding contact angle (θrec). An anisotropic CAH on a patterned surface can occur in either the direction perpendicular to a pattern, such as a groove or trench structure,[21,22] or in the direction parallel to a pattern, such as a tilted pillar structure.[3,23–26] Preferential droplet movement is subsequently observed in the direction exhibiting the lower CAH when the droplet is perturbed or stressed, such as through tilting the substrate or through vibrations of the substrate.

In the current work, asymmetrically textured surfaces in the form of arrays of tilted pillars are fabricated. The effects of the pillar size are explored in order to identify additional means to control droplet directionality through surface geometry. Our results indicate that changing the length scale of these surface features enables one to select the preferential directionality of droplets due to a switch in the direction exhibiting the lower contact angle hysteresis. We believe these findings will be valuable as part of the “toolbox” for controlling, manipulating, and tuning multiphase flows in 3-D systems. More specifically, they open up the possibility to transport droplets on the same chip in opposite directions merely by using patterns of two distinct length scales.

2. Results and Discussion

Arrays of tilted pillars were fabricated as a means to introduce asymmetry into one plane of the structured surface. Nanoscale diameter pillars were fabricated using a lithography-free...
method based on metal dewetting. Microscale diameter pillars were fabricated using common photolithography masking techniques. The fabrication method, shown schematically in Figure 1, resulted in arrays tilted nominally 30° off normal. After fabrication, the tilted arrays were silanized with a monolayer of trichloro(1H, 1H, 2H, 2H-perfluorooctyl)silane.

After fabrication, droplet transport on these ratchet surfaces was investigated. To induce motion, the chips with tilted pillar arrays (TPAs) were mounted onto the diaphragm of a speaker that was oscillated at 120 Hz. Droplets were released from just above the oscillating structured surface. The droplet impact and subsequent motion on the oscillating structured surfaces was recorded using a high speed camera. Directional motion was observed from droplets on all of the TPA surfaces. Surprisingly, the preferential direction of the motion switched when going from the nanoscale to the microscale structured surfaces. Droplets on the nanostructured surface moved in the same direction as the pillar tilt while droplets on the microscale surfaces moved in the opposite direction. The average horizontal velocities of the droplets are reported along with the surface characteristics in Table 1. The positive values of velocity indicate motion in the same direction as the feature tilt while the negative values indicate motion in the opposite direction of the feature tilt.

Snapshots of initial droplet impact and motion on the oscillating patterned surfaces are shown in Figure 2. The impact behavior changes from a complete rebound on TPA-1 to a more sticky impact on TPA-2 and TPA-3. On TPA-1, a droplet impacted the surface and rebounded in the same direction as the pillar tilt (Figure 2a). The directionality on TPA-1 is in agreement with prior reports where droplets preferentially moved in the same direction as the feature tilt on nanostructured surfaces. After the initial directional rebound, horizontal droplet motion on this superhydrophobic surface continued via a series of bounces, where each sequential bounce also had a directional rebound.

Snapshots of droplet impacts and subsequent motion onto the oscillating micropatterned surfaces are shown in Figures 2b,c. Droplets on TPA-2 and TPA-3 moved preferentially against the feature tilt. On the microscale patterned surfaces, droplet impact was followed by asymmetric depinning from the surface. The receding contact line depinning in the direction of the pillar tilt was slower than the receding contact line depinning against the pillar tilt. This asymmetric depinning moved the droplet preferentially against the surface.

Table 1. Characterization of water droplets placed onto the TPAs. The TPAs exhibit an asymmetric contact angle hysteresis (CAH) and asymmetric roll-off angles when the substrate is inclined with the pillar tilt versus when the substrate is inclined against the pillar tilt. The horizontal velocities were obtained from droplets impacting the structured surfaces attached to a vibrating speaker.

<table>
<thead>
<tr>
<th>TPA</th>
<th>Pillar Diameter (µm)</th>
<th>Pillar Height (µm)</th>
<th>Roll-off Angle a) (°)</th>
<th>Roll-off Angle b) (°)</th>
<th>CAH a</th>
<th>CAH b</th>
<th>Horizontal Velocity (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.20 (± 0.06)</td>
<td>1.1 (± 0.2)</td>
<td>4 (± 3)</td>
<td>28 (± 14)</td>
<td>4° (± 3°)</td>
<td>45° (± 12°)</td>
<td>11 (± 2)</td>
</tr>
<tr>
<td>2</td>
<td>1.0 (± 0.1)</td>
<td>1.6 (± 0.2)</td>
<td>11 (± 1)</td>
<td>8 (± 3)</td>
<td>16° (± 2°)</td>
<td>12° (± 3°)</td>
<td>−15 (± 3)</td>
</tr>
<tr>
<td>3</td>
<td>9.5 (± 0.5)</td>
<td>40 (± 5)</td>
<td>36 (± 4)</td>
<td>20 (± 1)</td>
<td>39° (± 3°)</td>
<td>27° (± 1°)</td>
<td>−24 (± 3)</td>
</tr>
</tbody>
</table>

a) Substrate inclined with the pillar tilt; b) Substrate inclined against the pillar tilt.
the pillar tilt. After the initial rebound, the droplet remained on the patterned surface (i.e., no additional bounces were observed). Horizontal droplet motion continued to proceed against the pillar tilt due to asymmetric depinning of the contact line forming the droplet footprint as the droplet moved alternately through advancing and receding motions with each oscillation of the structured surface.\[13,24,31,32\]

To understand this length scale dependent switch in directionality, the wetting properties of the tilted pillar arrays were investigated further. First, we analyzed the CAH values and corresponding roll-off angles for droplets placed onto the TPAs, as summarized in Table 1. Previous reports have indicated that asymmetrically patterned hydrophobic surfaces can exhibit an anisotropic CAH. This difference in CAH can then be employed to support directional water shedding.\[6,21\] In the current work, a clearly asymmetric CAH is observed on the TPAs when the substrate is inclined back and forth in the plane parallel to the feature tilt. Representative snapshots showing the droplets sitting on the patterned substrates when level, as well as when inclined are shown in Figure 3. Intriguingly, the direction exhibiting the lower CAH switches between the nanostructured surface, TPA-1, and in the opposite direction of the pillar tilt on the microstructured surfaces, TPA-2 and TPA-3.

![Figure 3. Sequence of images showing representative droplet impacts and subsequent directionality on patterned ratchet surfaces (a) TPA-1, (b) TPA-2, and (c) TPA-3. All chips have pillars tilted to the left and are mounted onto an oscillating speaker diaphragm, as shown schematically. The time is shown above the column. The dotted red lines are a guide to the eye to mark the center of impact and the arrows are a guide to the eye of droplet depinning. Horizontal droplet motion was observed in the same direction as the pillar tilt on the nanostructured surface, TPA-1, and in the opposite direction of the pillar tilt on the microstructured surfaces, TPA-2 and TPA-3.](image)

The CAH and values of the tilt angle at which the droplets roll-off the surface can be used to calculate the force acting on the water droplet just prior to roll-off, as well as the work of adhesion required to move a water droplet in contract with the surface (Figure 4).\[33\] When the droplet starts rolling, its weight balances the forces arising from contact hysteresis. The force acting on the droplet just prior to roll-off, $F$, can therefore be written as $F = \rho \Omega g \sin \alpha$, where $\rho$ is the density of water (1 kg/L), $\Omega$ is the droplet volume, $\alpha$ is the roll-off angle, and $g$ is the gravitational force. The work of adhesion arising from the contact hysteresis forces, $W_{adh}$, is the work required to move the contact line per unit area and can be written as $W_{adh} = \gamma \Delta \cos \theta$, where $\gamma$ is the surface tension of water (72.8 mJ/m²) and $\Delta \cos \theta = \cos \theta_{adv} - \cos \theta_{rec}$ (i.e. the contact angle hysteresis). Quantifying the directional work of adhesion as well as the force prior to roll-off enables a more intuitive analysis of the system. It also enables the different values collected during the tilt measurements such as the CAH as well as the roll-off angle to be used independently to characterize the system. For TPA-1, the nanostructured surface, the work of adhesion as well as the force at roll-on is lower when the surface is inclined with the pillar tilt than when the surface is inclined against the pillar tilt. The opposite trend is observed for TPA-2 and TPA-3. On these microstructured surfaces the work of adhesion as as well as the force at roll-off are both lower when the substrate is inclined against the pillar tilt rather than with the pillar tilt. In all cases, the preferential droplet directionality observed on vibrating ratchets follows the direction of lower CAH and lower adhesion relative to the pillar tilt.

Although the surface adhesion, roll-off angle, or CAH are intuitive means that are currently used to understand
preferential droplet directionality on the ratchet surfaces, they do not provide a microscopic picture of the interface between the water contact lines and the surface that is leading to this directionality. Recent work concluded that the receding contact line rather than the advancing contact line is the largest contributor to CAH and, therefore, droplet motion. While no rigorous theory is currently available to evaluate the CAH of structured surfaces such as those studied here, a detailed picture of the receding contact line on these surfaces is of great interest to better understand the root cause of the directional CAH. Here, two nonvolatile liquids were used to monitor the receding contact line of a droplet in a scanning electron microscope (SEM). Initially, cured optical adhesive was used to observe a single snapshot of the receding contact line. The substrate was tilted to let a droplet of optical adhesive slide a short distance and was then cured. In addition, 1-ethyl-3-methylimidazolium ethyl sulfate, was used to more closely approximate the composite interface formed between water and the structured surfaces. Several ionic liquids have been shown to produce θ and CAH very similar to that of water on several surfaces. 1-ethyl-3-methylimidazolium ethyl sulfate has a surface tension of 47 mN/m, which is within the same order of magnitude as water, and a viscosity similar to that of water. This ionic liquid exhibited θ_adv = 115° (±2°) and θ_rec = 94° (±2°) on a smooth surface. The θ and directional CAH of the ionic liquid have also been characterized on a structured surface, TPA-3, and are included as Figure S1. The values are comparable to those obtained with water in contact with the microstructured surface and confirm that a detailed picture of the receding contact line for the ionic liquid on the structured surfaces is comparable to that of water.

A representative SEM image of the optical adhesive on a microstructured surface is shown in Figure 5. The optical adhesive revealed that droplets resting on a microscale TPA were indeed in the Cassie-Baxter (CB) state. The formation of microcapillary bridges on the microscale TPAs was also observed, consistent with prior reports on microscale surfaces. Optical adhesive placed onto the nanostructured surface caused excessive bending and distortion of the nanopillars, and could not be analyzed further.

Placing a droplet of ionic liquid onto the structured surfaces allows for a magnified view of the contact line of the droplet on individual microstructured as well as nanostructured features, as shown in Figure 5a and Figure 6a. The droplets on both the nanostructured and representative microstructured surface are in a CB state, sitting on top of the pillars. This indicates that the change in directionality between the nanoscale and microscale features is not due to a change in wetting state associated with the length scale. Closer investigation of the images also reveals that the droplets are moving via the same capillary
bridge formation/rupture mechanism on both the nanostructured and microstructured surfaces. When a primary droplet detaches from a microstructure through the rupture of a capillary bridge, a satellite droplet is left behind.\cite{40, 42, 43} Prior work has attributed the measured hysteresis of a surface to the force required to break these microcapillary bridges.\cite{42} Satellite droplets are observed on the tops of several of the micropillars as well as several of the nanopillars. This indicates that movement of a droplet across the microstructured and nanostructured surfaces involves the same basic phenomena.

Since the droplet directionality is not related to a change in wetting state and is not controlled by a different mechanism at the different length scales, it is logical that the observed directionality is a direct result of the interplay between pillar geometry and Laplace pressure. The asymmetric geometry of the pillar has one edge with an overhang, which is reentrant, and one edge without an overhang, which is non-reentrant. Reentrant surface features typically discourage wetting where non-reentrant features promote wetting.\cite{44–49} This inhibition to wetting has made reentrant surface structures ideal for superhydrophobic as well as superoleophobic applications.\cite{44–49}

In the current work, the wetting on the sides of the pillar is asymmetric, with the water contact line pinned on the top of the pillar on the reentrant edge and pinned just below the edge of the top of the pillar on the non-reentrant edge. This asymmetry in pinning locations leads to asymmetric contact angles on each edge of the pillar, shown experimentally in Figure 5d and schematically in Figures 5e,f. Paxson et al.\cite{50} recently investigated the dynamic behavior of the receding contact line of a water droplet on microscale surface features using an environmental scanning electron microscope. Their work revealed a self-similar depinning mechanism indicating that the receding contact angle at each microstructured surface feature would reach a minimum value, corresponding to the intrinsic contact angle on a chemically equivalent smooth surface, before a microcapillary bridge would detach. When the contact line recedes on the asymmetric micropillars here, it is easier for depinning to start at the reentrant edge of the pillar than from the non-reentrant edge of the pillar because the angle there is closer to the critical angle required for capillary bridge necking and rupture (Figure 5e,f). This leads to preferential droplet directionality against the tilt of the microscale pillars. However, this mechanism does not explain the opposite directionality observed on the nanostructured surface where droplets were observed to move in the same direction as the feature tilt. It is likely that the Laplace pressure plays a larger role in the necking behavior at the nanoscale. Assuming a hemispherical droplet shape between adjacent pillars, the local radius of curvature on the microscale features in Figure 5c was approximately the diameter of the pillar. The same trend is assumed for the nanoscale features. The Laplace pressure, $P$, is then $\Delta P = \frac{2\gamma}{d}$, where $\gamma$ is the surface tension of water (72.8 mN/m) and $d$ is the diameter of the pillars. This leads to a pressure of 15 kPa for a droplet sitting on the microscale features on TPA-3 and 728 kPa for a droplet sitting on the nanoscale features on TPA-1. When the increased Laplace pressure due to the smaller radius of curvature of the droplet between the individual nanopillars combines with the asymmetric contact angle of the contact line, preferential depinning of the receding contact line occurs in the same direction as the feature tilt on the nanoscale. It is therefore the interplay between the Laplace pressure and the substrate geometry that enables the length scale of the pillars to switch the droplet directionality.

3. Conclusions

Arrays of tilted pillars ranging from the nanoscale to the microscale were fabricated and used as structural ratchets to directionally transport water at room temperature. Water droplets deposited onto the nanostructured ratchet move preferentially in the direction of the feature tilt while the opposite

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**Figure 4.** Directional (a) work of adhesion and (b) force acting on droplet just prior to roll-off for the structured TPAs when the substrate is inclined with the pillar tilt (blue) and against the pillar tilt (red).
Directionality is observed on the microstructured ratchets. This remarkable switch in directionality coincides with a switch in the direction exhibiting lower contact angle hysteresis and a lower work of adhesion relative to the pillar tilt. A nonvolatile ionic liquid deposited onto the pillar arrays was used to observe the contact line on the tilted pillar arrays in situ in a scanning electron microscope. This elucidated that an asymmetric contact angle forms on each side of the pillar due to a difference in wetting of the reentrant and non-reentrant pillar edges. This difference in contact angle leads to preferential depinning of the receding contact line in the opposite direction of the pillar tilt on microstructured surfaces. These results open up an elegant means to tailor transport directionality by tuning the size of asymmetric tilted pillar arrays of the same geometry and the same tilt angle. Directional control of droplet motion at room temperature would be advantageous for applications such as microfluidic devices, self-cleaning coatings, and directional adhesives.

4. Experimental Methods

Fabrication of Nanoscale Arrays: Fabrication of the tilted pillar array (TPA), shown schematically in Figure 1, was achieved with a lithography-free patterning method taking advantage of thin film dewetting. A 10 nm to 15 nm thick layer of platinum (Pt) was deposited onto a single side polished single crystal silicon (Si) wafer (100) with 100 nm of thermally grown silicon oxide (SiO₂) using physical vapor deposition in a vacuum evaporator equipped with an electron gun source (Thermonics Laboratory, VE-240). Wafers with a Pt layer were then thermally processed at ≈ 850 °C for 8 seconds in a mixture of argon and hydrogen (10:1) at a pressure of 735 Torr in a cold wall furnace (Easy Tube 3000, First Nano, Ronkonkoma, NY) equipped with a radiative heat source set to its maximum power (22 kW). The resulting dewet Pt layer then served as a mask during anisotropic reactive ion etching (RIE) of the SiO₂ and Si. The RIE was carried out in an Oxford PlasmaLab system (Oxford Instruments, UK) using glancing-angle RIE with the wafer sitting on an aluminum holder bent to an angle of 70° relative to the surface of a silicon carrier wafer. A perfluorinated oil (Fomblin 25/5) was placed between the wafer and the aluminum holder to ensure even heat transfer during etching. The 100 nm of SiO₂ was etched in a mixture of C₄F₈ and O₂ at flow rates of 45 sccm and 2 sccm, respectively, at 15 °C, 7 mTorr for 55 s. The anisotropic etching of Si was carried out at 10 mTorr in a SF₆:C₄F₈:Ar mixture defined by respective flow rates of 56, 25, and 5 sccm. Organic contaminants encountered during fabrication were removed from the nanopillar arrays with an O₂ plasma, resulting in superhydrophilic surfaces. The nanopillar dimensions and tilt angle were determined using a scanning electron microscope (Carl Zeiss, Merlin).

Fabrication of Microscale Arrays: Fabrication of the microscale arrays was achieved through conventional photolithography. A single side...
polished single crystal Si wafer (100) with 100 nm of thermally grown SiO$_2$ was used as a starting material. A 0.7 µm thick film of a negative photoresist (NFR, Doe & Ingalls of North Carolina) was used to form an array of squares that were 10 µm or 40 µm in diameter. After exposure, the photoresist was developed using CD-26. The resulting patterns were etched with glancing-angle RIE. The 100 nm of SiO$_2$ was etched using a mixture of C$_4$F$_8$ and O$_2$ at flow rates of 45 sccm and 2 sccm, respectively, at 15 °C, 7 mTorr for 55 s. The anisotropic etching of Si was performed with Bosch etching. The Bosch etching consists of sequential deposition and etch steps. The deposition step has a mixture of SF$_6$ and C$_4$F$_8$ at flow rates of 1 sccm and 140 sccm, respectively, at 15 °C, 20 mTorr for 4 s. The etch step has a mixture of SF$_6$ and C$_4$F$_8$ at flow rates of 120 sccm and 1 sccm, respectively, at 15 °C, 20 mTorr for 5 s. The number of iterations determines the etch depth and therefore feature height. After the desired feature height was obtained, the photoresist mask and any organic contaminants encountered during fabrication were removed with an O$_2$ plasma, resulting in superhydrophilic surfaces.

Smaller 1 µm diameter circular features were also patterned using a double layer of LOR A (Micro Chem) under a positive photoresist (MEGAPOSIT™ SPR 955-CM, The Dow Chemical Company). After development, chromium was deposited into the circular holes. The excess photoresist and metal was removed using an acetone bath followed by a mix of N-methyl-2-pyrrolidone (70°C, 20 min). The metal pattern was etched with glancing-angle RIE following the same recipes used for the larger diameter microscale arrays. After etching, the metal mask was removed using a chromic photomask etchant (Cr-145) bath for 2 min. An O$_2$ plasma was used to remove any organic contaminants encountered during fabrication.

**Functionalization of the TPAs:** After fabrication, all of the TPAs were silanized with trichloro(1H, 1H, 2H,2H-perfluorooctyl)silane (Sigma-Aldrich). Silanization was performed by placing 20 µL of the silane into a petri dish containing the substrates. The petri dish was then heated to 80°C for 1 h.

**Droplet Motion Experiments:** The chips were mounted onto the diaphragm of a speaker (HiWave BMR12 2” Compact Full-Range speaker) that was driven by a function generator capable of up to 10 V output amplitude (Standford Research Systems, Model DS345). Droplet impact and motion experiments were conducted on all of the TPAs. These experiments were performed with deionized water on a leveled surface and a high speed camera (EPIX X-Cap LTD V3.7, Sun Microsystems, Inc.) to record the droplet trajectory and velocity. Droplets of a constant volume (8 µL) were dispensed with a syringe pump (Harvard Apparatus, Pump II Pico Plus Elite) leading to droplets with diameters of 2.5 mm. The height that the droplet was released from was controlled using a micrometer to maintain a constant Weber number (We) of = 2. The Weber number compares inertial effects to the surface tension of a droplet:

$$\text{We} = \frac{\rho V^2 D}{\sigma}$$

where $\rho$ is the density of the liquid (1000 kg/m$^3$), $V$ is its impact velocity, $D$ is the droplet diameter, and $\sigma$ is the surface tension (72.8 mN/m for water). Oscillation of the TPAs was driven by a speaker set to 120 Hz with an amplitude of 1 V. A range of frequencies were investigated with droplets either sitting still or moving directionally as described in the text. To evenly compare the surfaces, the horizontal droplet velocity on the different surfaces was quantified at a single frequency and amplitude. Horizontal droplet trajectory and velocity were obtained by analyzing the recorded videos (1019 frames per second) with Imagej (NIST, Version 1.45r) and monitoring the centroid position in each successive frame. At least five droplets were tracked for each surface to obtain the average velocities presented.

**Wetting at Room Temperature:** The water contact angle and contact angle hysteresis just before droplet roll-off were characterized at ambient temperature with a goniometer (Ramé-Hart Instrument Co., Model 590 F4 series with DROPiTmage Advanced V2.5). The contact angle hysteresis of five 5 µL droplets was analyzed to obtain an average.

**Visualization of Contact Line on Surface Features:** Two nonvolatile liquids were used to image the contact line as it touches the surface features. The first was a UV curable adhesive NOA 73 (Norland Products Inc.). One droplet of the optical adhesive was placed onto the structured surfaces. The surface was then manually tilted to approximately 45° to allow the droplet to slide. The adhesive was then cured with exposure to ultraviolet light for 25 s. The cured liquid sitting on top of the pillars was imaged under vacuum in a SEM. The adhesive visibly damaged the nanopillar arrays. Therefore, an ionic liquid, 1-ethyl-3-methylimidazolium ethyl sulfate (Sigma-Aldrich), was used to see the contact line on the pillars in situ. A 2 µL droplet of the ionic liquid was placed onto the pillar array and then imaged under vacuum in the SEM. The various images were obtained by placing the structured surface on a sample holder cut at a 45° angle. When mounted, the pillar tilt was perpendicular to the stage tilt in most cases. Inside the SEM, the stage was rotated and/or tilted up to an additional 35° to better view the interface between the liquid and the surface or to induce motion of the droplet. The ionic liquid is nonvolatile and can therefore be imaged in situ without any curing. Care was taken to prevent electrowetting of the ionic liquid across the structured surfaces due to a high dose from the electron beam.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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