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## Minimization of Free Volume: Alignment of Triptycenes in Liquid Crystals and Stretched Polymers\*\*

By Timothy M. Long and Timothy M. Swager\*

Many emerging technologies require new methods to control supramolecular order through design of complementary structures on a molecular scale. Electrostatic interactions, chelation, and hydrogen bonding have dominated these designs, producing a variety of receptors, electroactive, and catalytic materials.<sup>[1]</sup> However, the use of the minimization of free volume and van der Waals interactions have received little attention for supramolecular design beyond crystal engineering.<sup>[2]</sup> Triptycenes and other fused bicyclic systems, due to their rigid three-dimensional molecular structure, have free volumes swept out by their aromatic faces. Herein, we define “internal free volume” as the volume defined by the rigid aromatic faces of the triptycene as shown in Figure 1.

This volume exists because the triptycene structure cannot obtain any fully co-planar molecular orientation. We have

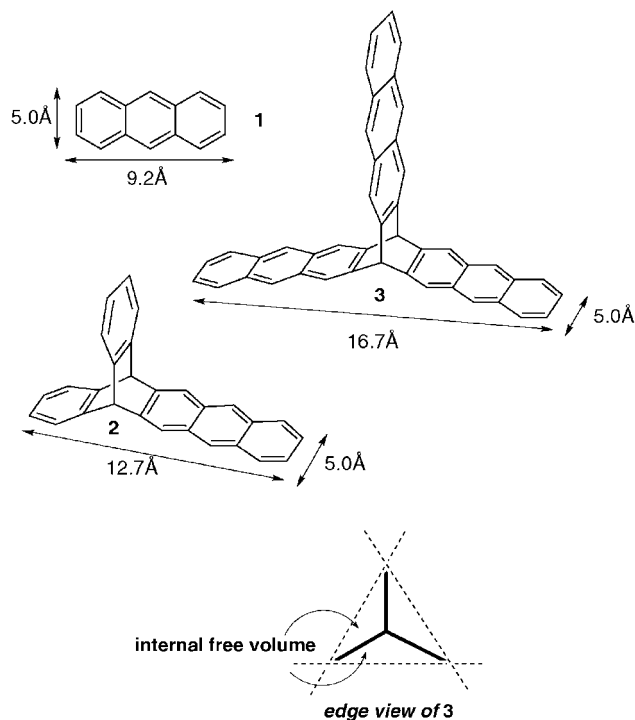


Fig. 1. Structures and dimensions of 1–3 with definition of “internal free volume”.

previously used these voids within pentiptycene to prevent polymer aggregation and increase solid-state fluorescence quantum yields for development of a highly fluorescent chemosensor to detect trinitrotoluene (TNT) vapors.<sup>[3]</sup> The voids can also provide a unique opportunity to produce novel supramolecular structures through appropriate host selection, such as liquid crystals (LCs) and polymers. Crystals of such compounds have yielded solvent clathrates or co-crystals with small electron deficient molecules, such as benzoquinone<sup>[4]</sup> and NO,<sup>[5]</sup> or the much larger C<sub>60</sub>.<sup>[6]</sup>

In this communication, we report a unique supramolecular assembly involving blends of selected triptycene derivatives in LCs and polymer films. Compounds **1**, **2**,<sup>[7]</sup> and **3** (Fig. 1), containing 2,3-anthracenyl groups, were introduced into a room temperature nematic LC. It has been shown that small aromatic guest molecules will align in nematic liquid crystalline solvents or uniaxially stretched polymer sheets.<sup>[8]</sup> In most studies, alignment proceeds such that the director axis of the nematic liquid crystal or stretching direction of a polymer film is parallel, on average, to the long-axis of the guest molecule. This effect can be visualized through polarized ultraviolet-visible (UV-vis) and infrared (IR) spectroscopies.<sup>[9]</sup> Polarized UV-vis spectra of **2** and **3** were compared with anthracene (**1**), which is known to align according to its aspect ratio; thereby the anthracenyl-group was used as a probe of molecular orientation.<sup>[10,11]</sup> The aspect ratio for each of the three molecules<sup>[12]</sup> is defined by the ratio of their longest to shortest axes and is 1.84 for **1**, 2.54 for **2**, and 3.34 for **3**. Based upon simple aspect ratio considerations, alignment of the long axis of each molecule will be along the host alignment direction, and should increase across the series from **1** to **3**. More complex treat-

[\*] Prof. T. M. Swager, T. M. Long  
 Department of Chemistry  
 Massachusetts Institute of Technology  
 77 Massachusetts Ave., 18-209, Cambridge, MA 02139 (USA)  
 E-mail: tswager@mit.edu

[\*\*] The authors thank the National Science Foundation and the Office of Naval Research (ONR) for generous financial support.

ments for prediction of solute ordering in LCs report this free-volume guided alignment.<sup>[13]</sup> In particular, the surface-tensor approach based on solute/solvent shape alone of Ferrarini and co-workers predicts this sense of alignment.<sup>[13a]</sup> However, to this point, no practical example to support these theoretical predictions has been demonstrated.

Homeotropic alignment of 1 wt.-% mixtures of **1–3** in 4-(*trans*-4-pentylcyclohexyl)benzointrile was achieved using surface rubbed test cells to give uniaxial alignment. Polarized spectra of **1** in the nematic LC were consistent with previous literature reports, showing alignment of the molecules, on average, with their long axes along the nematic LC director.<sup>[11]</sup> The transition moment of the lowest energy vibronically coupled absorption (320–380 nm) of **1** is short-axis polarized, and therefore gives, in agreement with an aspect-ratio alignment mechanism, larger UV-vis absorption with light polarized perpendicular to the LC director.<sup>[9a]</sup> Observation of the polarization dependence of the similar absorption bands of the anthracenyl-moieties of **2** and **3** allowed for detection of their orientation. The clearing point of solutions of **3** decreases steadily upon increased solute concentration from 50.0 °C (0.5 wt.-%) to 48.7 °C (4 wt.-%; 51.6 °C blank LC solution; see Experimental.

Upon measurement, the dichroic ratio of mixtures of **2** and **3** were found to be the inverse of **1** (Fig. 2a,b); the dichroic ratio,  $A_{\parallel}/A_{\perp}$  for **1–3** are listed in Table 1 along with associated order parameters using the short-axis transition. Note that for **2** and **3**,  $A_{\parallel}/A_{\perp}$  are >1.0 while for **1**,  $A_{\parallel}/A_{\perp}$  is < 1.0. Larger absorptions (320–380 nm) were seen when exposed to parallel polarized light versus perpendicular. This can be most easily seen in the 0–0 absorption at 380 nm that is purely short-axis polarized. The higher energy vibronically coupled absorptions begin to overlap a higher energy long-axis polarized transition. Variable temperature UV-vis spectroscopy (data in Experimental section) on a 1 wt.-% solution of **3** showed a steady decrease in order parameter until the clearing point of the LC was reached. Upon cooling back into the nematic phase, alignment of **3** reemerges with decreased temperature. Decreasing the concentration of **3** to 0.5 wt.-% had no effect on the order parameter.

The observed dependence implies that the average alignment of the anthracene chromophores of the triptycenes is

Table 1. Dichroic ratios for **1–3** in aligned hosts [a].

Compound, Host	Long-Axis $A_{\parallel}/A_{\perp}$	Short-Axis $A_{\parallel}/A_{\perp}$	$S$ [c]
<b>1</b> , LC	-	0.66 [b]	-0.13
<b>1</b> , PVC	1.04	0.93 [b]	-0.04
<b>2</b> , LC	-	1.80	0.14
<b>2</b> , PVC	0.83	1.56	0.17
<b>3</b> , LC	-	2.34	0.31
<b>3</b> , PVC	0.77	1.56	0.15

[a] UV maxima for each dichroic ratio measurement were (long-axis, short-axis/nm): **1** (257, 381), **2** (263, 379), **3** (282, 383). [b] For direct comparison of absorption intensities with **2** and **3**, the inverse of these ratios should be taken. For LC,  $A_{\perp}/A_{\parallel}$  = 1.52; poly(vinyl chloride) (PVC)  $A_{\perp}/A_{\parallel}$  = 1.07; note these are both smaller than values for **2** and **3** in all cases. [c] Calculated using short axis absorbances.

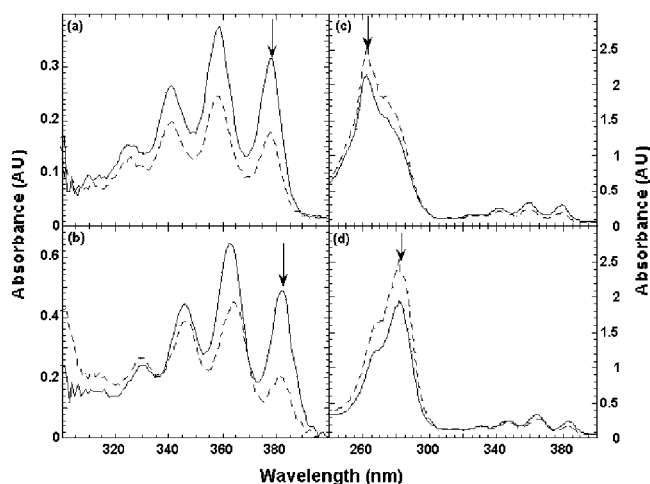


Fig. 2. a) UV-vis absorption spectra of **2** in homeotropically aligned 4-(*trans*-4-pentylcyclohexyl)benzointrile LC; b) UV-vis of **3** in same. (Solid = parallel to LC director; dashed = perpendicular to LC director; arrows indicate points used for dichroic ratio measurements); c) UV-vis absorption spectra of **2** in uniaxially stretched PVC. d) UV-vis of **3** in same. (Solid = parallel to stretching; dashed = perpendicular to stretching; arrows indicate points used for dichroic ratio measurements).

normal to the LC director, resulting in an alignment that is the opposite expected from aspect ratio considerations alone. We attribute this novel alignment to the free volume of the iptycene molecules. Based on this argument, **3** is expected to align the most efficiently since it traces out larger void spaces due to its size. On the other hand, **2** would be expected to align, but poorly. Nevertheless, it was seen to align well, as even the smaller void spaces created by **2** are sufficient to align molecules showing the powerful effect of free volume spaces coupled with a rigid backbone.

We propose that the most efficient packing is best accomplished by a “threading” mechanism wherein the LC packs within the iptycene void spaces as depicted in Figure 3b. This observed solvation should fill the empty spaces created by the iptycenes while minimally disrupting alignment of the host. As can be seen in Figure 3a, the opposite, aspect-ratio align-

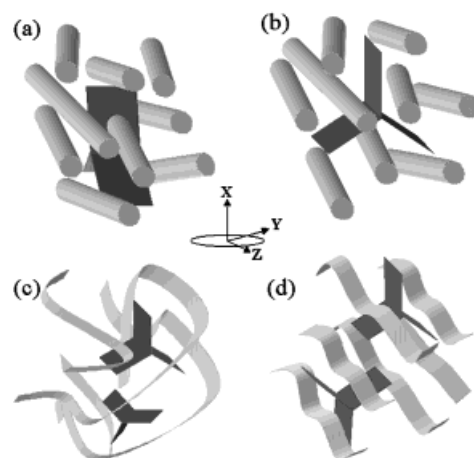


Fig. 3. a) Aspect ratio alignment of triptycenes in LCs. b) Proposed “minimization of free volume” alignment of triptycenes in LCs. c) Orientation of triptycenes in polymer blend before stretching. d) Proposed alignment of triptycenes in stretch-aligned polymer.

ment does not efficiently fill the voids, and would cause a greater disruption to the nematic phase. Some small, bridged binaphthol derivatives have been shown to align similarly in LC hosts; however, molecular projections along the LC director show they trace out much smaller, offset voids similar to triptycenes but are not as conformationally rigid. This results in zero free volume and these structures can best be described as disk-like. Extended 6,6'-binaphthol derivatives were found to align according to aspect ratios.<sup>[13c]</sup>

As a further demonstration of the generality of these interactions in the "threading" model, thin solution-cast poly(vinyl chloride) films containing 1 wt.-% **1–3** were prepared. These were then uniaxially stretched to impart macromolecular alignment.<sup>[14–16]</sup> If the alignment is guided by the shape complementarity of the solute and solvent, then changing from LCs to polymers should yield the same results. No theoretical treatment of solute alignment in stretch-aligned polymers beyond aspect-ratio considerations has been described.

The enlarged UV-vis window of poly(vinyl chloride) versus the LC allows observation of both the strong anthracene absorption at 250 nm as well as the weak 350 nm absorption. As with the LC host, **1** aligns with its long axis along the stretching direction, while **2** and **3** both show a preference for alignment of their long axes normal to the stretching direction (Fig. 2c,d). This can be seen in both absorptions at 260 nm and 380 nm as they have an inverse relationship with respect to the incident polarization. This alignment is analogous to the LC case where, in this case, as stretching aligns the polymer host from an amorphous state (Figure 3c) to a uniaxial state (Figure 3d), the chains of the polymer thread through the void space. The alignment is reflected in the dichroic ratios listed in Table 1. In all cases, the alignment provided by the uniaxial poly(vinyl chloride) was lower than that achieved by LC alignment.

Herein, we have shown that the unique three-dimensional structures of triptycenes result in special solvation properties, which can be used to create unique solute orientations. In order to prevent the formation of a vacuum, the internal free volume between the three aromatic triptycene faces allows for the threading of LCs through these spaces. We, therefore, have demonstrated a first and reliable scaffold, which supports the surface tensor model for alignment in LCs based on molecular shape. Moreover, we illustrated the generality of this threading by also using a stretched polymer to illicit the same alignment sense. This interaction sense causes an unusual alignment of chromophores that are part of the iptycene backbone. Use of larger triptycenes homologues could ultimately allow for isolation of individually and homogeneously aligned polymer bundles or chains, producing materials with unique physical properties. Extension of this methodology to larger iptycene frameworks could potentially allow for the construction of polymer blends wherein the two component polymers are aligned mutually perpendicular to each other. Such alignment would create a very low density network, which should be mechanically very strong. Such extension is currently under investigation.

## Experimental

**Chemicals:** Anthracene (**1**) was purchased from Aldrich Chemical Co. and recrystallized from methanol before use. Compound **2** was prepared according to the literature procedure [7]. Compound **3** was prepared as described below. Poly(vinyl chloride) ( $M_n = 99\,000$ , polydispersity index (pdi) = 2.35) and 4-(*trans*-4-pentylcyclohexyl)benzonitrile were obtained from Aldrich Chemical Co. and used as received. All synthetic manipulations were performed under an argon or nitrogen atmosphere unless otherwise noted.

**Instrumentation:** UV-vis spectra were recorded on a Cary 50 or Hewlett Packard 8453 UV-vis Spectrophotometer. The polarizer was an Oriel Instruments 27320 UV Linear Dichroic Polarizer loaded in an Oriel 25010 Polarizer Rotator. Variable temperature UV-vis spectra were taken using the Cary 50 fiber optic probe accessory. The temperature was adjusted by mounting the test cell in a Mettler FP 82 HT hot stage and a Mettler FP 80 HT central processor and equilibrated for 15 minutes before measurement. Transition temperatures were determined at scan rates of 5 °C/min by differential scanning calorimetry using a Perkin-Elmer DSC 7 with a Perkin-Elmer 7700 thermal analysis data station. Liquid crystal test cells were 10 μm wide, polyimide coated, and parallel rubbed (0°) from E.H.C. Co. Ltd, Tokyo, Japan. High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry Instrumentation Facility (DCIF) using a peak-matching protocol to determine the mass and error range of the molecular ion.

Table 2. Differential scanning calorimetry (DSC) data for mesophase behavior as a function of wt.-% solute [a].

Solute [wt.-%]	$T_m$ [°C]	$T_{clear}$ [°C; heating]	$T_{clear}$ [°C; cooling]
<b>1</b> ; 0.5	26.2	51.4	50.3
<b>1</b> ; 1.0	25.7	51.3	50.1
<b>1</b> ; 2.0	25.2	50.9	49.8
<b>1</b> ; 4.0	25.0	50.5	49.1
Blank LC	25.4	51.7	50.5
<b>3</b> ; 0.5	26.3	50.1	49.4
<b>3</b> ; 1.0	25.7	49.4	48.8
<b>3</b> ; 2.0	26.6	48.9	48.0
<b>3</b> ; 4.0	25.9	48.7	46.4

[a] Temperatures are uncorrected, measured at 5 °C/min heating rate, and reported as onset values.

**Liquid Crystal Studies:** A solution of 0.25 g of 4-(*trans*-4-pentylcyclohexyl)-benzonitrile and 2.5 mg analyte in chloroform was prepared. The chloroform was then removed in vacuo to yield the desired liquid-crystal solution that was then dried overnight in vacuo, protected from light. Alternatively, a mixture of analyte and liquid crystal were heated, stirred in the isotropic phase until homogeneous, and cooled. Both preparations yielded the same results. Liquid crystal test cells were then prepared by heating the solution, until it became isotropic, and loading it into a warm cell via capillary action. The cells were then allowed to cool slowly to room temperature and their polarized spectra were recorded. The liquid crystal mixtures were examined by polarized optical microscopy. The mixtures exhibited no evidence of phase separation or microcrystallization.

**Polymer Studies:** A solution of 0.25 g poly(vinyl chloride) and 2.5 mg analyte were dissolved in 30 mL 1,2-dichloroethane and heated to 80 °C for one hour to completely dissolve the polymer. The hot solution was then poured into a petri dish (9 cm diameter) and allowed to dry slowly overnight. The film was then peeled from the dish, cut into strips, and uniaxially stretched with a mechanical stretcher at 90–110 °C (above the  $T_g$  of poly(vinyl chloride)) to a stretching ratio of 6–8.

Table 3. Order parameter of **3** as a function of temperature [a].

Temperature [°C]	S
30 (heating)	0.30
40 (heating)	0.27
55 (heating)	0.03
45 (cooling)	0.21
35 (cooling)	0.22
30 (cooling)	0.24

[a] 1 wt.-% solution; 15 min equilibration time between measurements.

**Preparation of 7,16-(2',3'-anthraceno)-7,16-dihydroheptacene (3):** 90.0 g  $\text{AlCl}_3$  was added in small portions at 0 °C and under Ar to a mechanically stirred solution of 19.05 g (75 mmol) triptycene and 36.70 g (225 mmol) phthalic anhydride in 1 L tetrachloroethylene. After complete addition, the cooling was removed and the mixture was heated to 100 °C for 20 h. The solution was cooled and poured into 750 mL of an ice/5 % aqueous HCl solution and stirred for one hour. The solids were then collected by vacuum filtration and dissolved in 10 % aqueous NaOH. The basic solution was filtered and acidified to pH 1. The resulting solids were filtered, washed with water, and dried in vacuo to give the tris-ketoacid derivative, **A**, as an off-white (pink to tan) solid, which is used without further purification.

A solution of **A** (from above) in 1 L concentrated sulfuric acid was heated to 100 °C for 17 h, cooled, and poured into 3 L crushed ice. The resulting solids were collected by filtration, washed with water, and dried under vacuum. The solids were then heated three times in 1.5 L boiling chloroform, and filtered. The organic solutions are combined and concentrated in vacuo. This solid was adsorbed on to silica and subjected to flash chromatography with 1:1 chloroform/dichloromethane to give 6.31 g, 13 % yield (two steps), of the wholly symmetric **B** ( $R_f = 0.06$ ):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.44$  (s, ArH, 6H), 8.27 (dd, ArH,  $J = 6.0, 3.3$  Hz, 6H), 7.78 (dd, ArH,  $J = 5.7$  Hz, 3.5 Hz, 6H), 6.15 (s, CH, 2H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 182.7, 148.1, 134.4, 133.4, 132.6, 127.5, 123.2, 54.4$ ; FT-IR(KBr):  $\nu/\text{cm}^{-1}$ : 3056, 1673, 1617, 1594, 1322, 1288, 959, 720; HRMS (EI): Calcd. for  $\text{C}_{44}\text{H}_{20}\text{O}_6$  (M+) 644.125989, found 644.1270  $\pm$  0.0019. M.p. > 300 °C.

7.0 g Al and 1.0 g  $\text{HgCl}_2$  were placed in a 500 mL Schlenk flask under Ar. 150 mL freshly distilled cyclohexanol (from Na) was added and the mixture was refluxed for one day in the dark. The solution was cooled below reflux temperature and 4.875 g (75.6 mmol) of **B** was added, followed by an additional 110 mL cyclohexanol, and the solution was heated back to reflux temperature for an additional day. The solution was then cooled, and the majority of the cyclohexanol was removed by distillation under vacuum to give a gummy green solid. A large volume of water was added to the solid and the solution was extracted with chloroform. The combined organic layers were washed with water and saturated NaCl (aq.), dried over  $\text{MgSO}_4$ , and concentrated in vacuo to give a suspension of solid in cyclohexanol. Addition of a ten-fold excess of methanol caused the precipitation of a crude solid, which was isolated by filtration. Column chromatography of the crude solid on neutral alumina with 2:1 hexane/dichloromethane gives a pale yellow solid, which can be recrystallized from hexane/dichloromethane to yield small needles of **3** ( $R_f = 0.44$ ), 0.75 g (18 % yield).  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.30$  (s, ArH, 6H), 8.05 (s, ArH, 6H), 7.93 (dd, ArH,  $J = 6.4, 3.3$  Hz, 6H), 7.39 (dd, ArH,  $J = 6.6, 3.3$  Hz, 6H), 5.83 (s, CH, 2H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 139.9, 131.8, 131.0, 128.2, 126.0, 125.2, 122.1, 53.3$ ; UV ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}/\text{nm}$  (log $\epsilon$ ): 281 (5.44), 329 (4.07), 345 (4.28), 363 (4.37), 381 (4.15); FT-IR(KBr):  $\nu/\text{cm}^{-1}$ : 3038, 2998, 2949, 2925, 2852, 1677, 1426, 1296, 900, 738, 470; HRMS (EI): Calcd. for  $\text{C}_{44}\text{H}_{26}$  (M+), 554.203451, found 554.2021  $\pm$  0.0016. M.p. > 300 °C.

Received: September 1, 2000  
Final version: December 12, 2000

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were optimized using semiempirical calculations (PM3). Distances were then measured as proton–proton centroid distances as shown in Figure 1.

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## Fabrication of Nanometer-Scale Features by Controlled Isotropic Wet Chemical Etching\*\*

By J. Christopher Love, Kateri E. Paul, and George M. Whitesides\*

This paper describes the application of a historically well-known phenomenon in lithography—undercutting by isotropic wet etching<sup>[1,2]</sup>—for the fabrication of nanostructures. We have combined conventional photolithography with simple isotropic wet etching to transfer the edges of a photoresist pattern into an underlying thin metal film by a two-step process. We etch isotropically, with controlled undercutting, through a thin metal film supported on a substrate of Si/SiO<sub>2</sub> or CaF<sub>2</sub>. Subsequent deposition of a second thin metal film, followed by lift-off, defines trenches at the edges of each photoresist feature. This technique is an example of “edge lithography”, a form of lithography in which the edges of the original pattern become the features of the final pattern. This technique generates structures with critical dimensions as small as 50 nm in a thin film of chromium or aluminum. The roughness of the edges produced is ~10–15 nm, and is limited theoretically to the grain size of the metal layer.

Convenient, inexpensive techniques for patterning features with nanometer-scale dimensions from the top down are an important component of nanoscience. In the short term, methods for producing nanometer-scale features that are already highly developed—DUV (deep ultraviolet), electron-beam (e-beam) writing, EUV (extreme ultraviolet), and X-ray photolithography<sup>[3,4]</sup>—will provide the basis for commercial production of microelectronic devices with features <100 nm. Fabrication of structures with nanometer-scale features appropriate for conducting exploratory research, for prototyping, and for fabricating simple devices are usually prohibitively expensive using advanced lithographic techniques; there is, therefore a place for simple methods that do not have the stability and reproducibility required for the fabrication of

[\*] Prof. G. M. Whitesides, J. C. Love, K. E. Paul  
Department of Chemistry and Chemical Biology  
Harvard University  
Cambridge, MA 02138 (USA)  
E-mail: gwhitesides@gmwhgroup.harvard.edu

[\*\*] This research was supported by DARPA/AFRL/SPAWAR and used the MRSEC Shared Facilities supported by the NSF under Award No. DMR-9809363. JCL gratefully acknowledges the DoD for support in the form of a graduate fellowship. The authors thank Stephen Shepard and Yuanzhang Lu for their technical assistance.