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Organizing Carbon Nanotubes with Liquid Crystals

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ABSTRACT

Single- and multiwalled carbon nanotubes dispersed in nematic liquid crystal (LC) solvents are found to be orientationally ordered by the nematic matrix. Procedures are demonstrated for the preparation of monolayer and multilayer nanotube films with organization controlled using well-established methods of LC alignment, including grooved surfaces, magnetic fields, and patterned electrodes. LC alignment should be possible with other nanometer-sized building blocks, offering a general route for controlled assembly of organized nanomaterials and devices.

Over the past two decades a wide range of new nanometer-scale particles have been discovered and characterized, ranging from semiconductor and metal clusters and quantum dots, to fullerenes and self-assembled supramacromolecular aggregates. These molecules and nanoparticles are the basic components from which emerging and future nanotechnologies will be constructed. The next step toward preparing useful materials and functional devices is to devise processing strategies enabling the controlled assembly of such components into larger structures with engineered order. Many applications envisioned for nanoscale building blocks require post-synthesis manipulation under relatively mild conditions to enable integration with electrodes, actuators, and other device elements. Post-synthesis strategies for organizing nanoparticles include self-assembly directed by specific interparticle interactions,[1] templating by patterned substrates[2] or on the surfaces of larger particles,[3] mechanical ordering,[4] and electric fields.[5]

Methods for organizing single- and multiwalled carbon nanotubes (SWCNT and MWCNT) are of particular interest because these materials are especially promising building blocks for so many applications.[6] Although several approaches have been developed for aligning carbon nanotubes (CNT) during growth,[7−9] methods for post-growth manipulation and alignment are awkward, incompatible with microscopic patterning, or restricted to a narrow range of size scales.[10,11] Here we report that thermotropic liquid crystals (LC) used as solvents provide a simple yet versatile and reproducible way to control order in SWCNT and MWCNT films. The key finding is that CNTs in nematic media orient parallel to the director (where the director is defined as the axis of average LC molecule orientation). This enables preparation of monolayer and multilayer films with orientation controlled using well-established methods of LC alignment, including grooved surfaces, magnetic fields, and patterned electrodes. Using these approaches we demonstrate straightforward methods for connecting pairs of electrodes with CNT wires, and for the formation of uniaxial and biaxial SWCNT and MWCNT films, ordered over a range of length scales and film thicknesses. LC alignment should be possible with other nanometer- to micron-sized building blocks, offering a general route for controlled assembly of organized nanomaterials and devices.

Organized SWCNT and MWCNT films were prepared by dispersing CNTs in a LC host via ultrasonication and depositing them onto a porous polycarbonate membrane substrate (Millipore Isopore or Nuclepore 100 or 200 nm pore size), as shown schematically in Figure 1.[12] A droplet was placed on the membrane and drawn slowly through the pores with a mild vacuum. Most CNTs remained adsorbed to the surface of the membrane. Additional droplets could be added sequentially, increasing film thickness as desired. The membranes were covered with shallow parallel scratches which resulted in planar alignment of the LC solvent parallel to the grooves but did not interfere with CNT adsorption or imaging. Two thermotropic LCs were used in this study: 4′-pentyl-4-cyanobiphenyl (5CB, nematic range 24−35 °C), and E7, a mixture of alkyl- and alkoxycyanobiphenyls (nematic range −10 to +60 °C).[13] Comparable results were obtained for both LCs. LCs are poor solvents for CNTs, so suspensions had to be used soon after preparation to prevent flocculation. Once films were deposited, they were imaged by atomic force microscopy (AFM) without further treatment.

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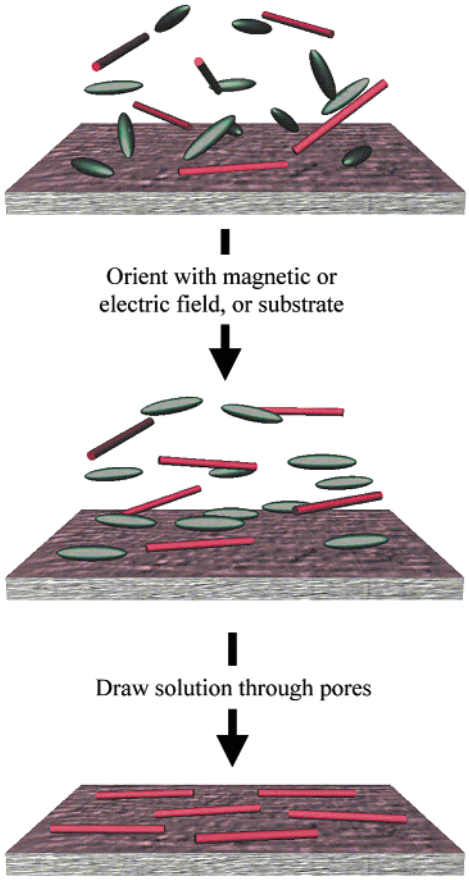

Figure 1. Organizing CNTs with LC solvents. (a) A droplet of liquid crystal (ellipsoids) with suspended carbon nanotubes (rods) is applied to a porous membrane substrate. (b) The bulk LC is then aligned using a grooved surface or external field, which in turn orders the nanotubes. (c) The LC is drained through the porous membrane leaving behind an ordered nanotube film.

Figure 2 presents representative AFM images of SWCNT and MWCNT films deposited from LCs onto polycarbonate membranes. The grooves, as well as the nematic director, were oriented vertically in the figure, as determined separately by optical microscopy. The majority of CNTs oriented parallel to this axis, with alignment quality nearly independent of coverage, up to films several layers thick. The degree of order in such films equaled or surpassed that offered by any other means yet reported for post-growth CNT alignment.

As discussed below, LCs can be used to control both short- and long-range order in CNT films. To quantify the amount of long-range order, alignment statistics were measured for MWCNTs at widely spaced locations on several samples. Some results are presented in Figures 3a−c. The data are summarized using the two-dimensional orientational order parameter $S = \langle 2\cos^2\phi - 1 \rangle$, where ϕ is the angle between a particular particle and the mean orientation of all particles, and the brackets denote an average over all observations. $S = 0$ for random alignment and 1 for perfect order. In samples prepared at room temperature, near the center of the LC solvent's nematic range, the order parameter was typically $0.7 \sim 0.9$ when substrate grooves were used to align the LC. Some films were prepared with 5CB in its isotropic

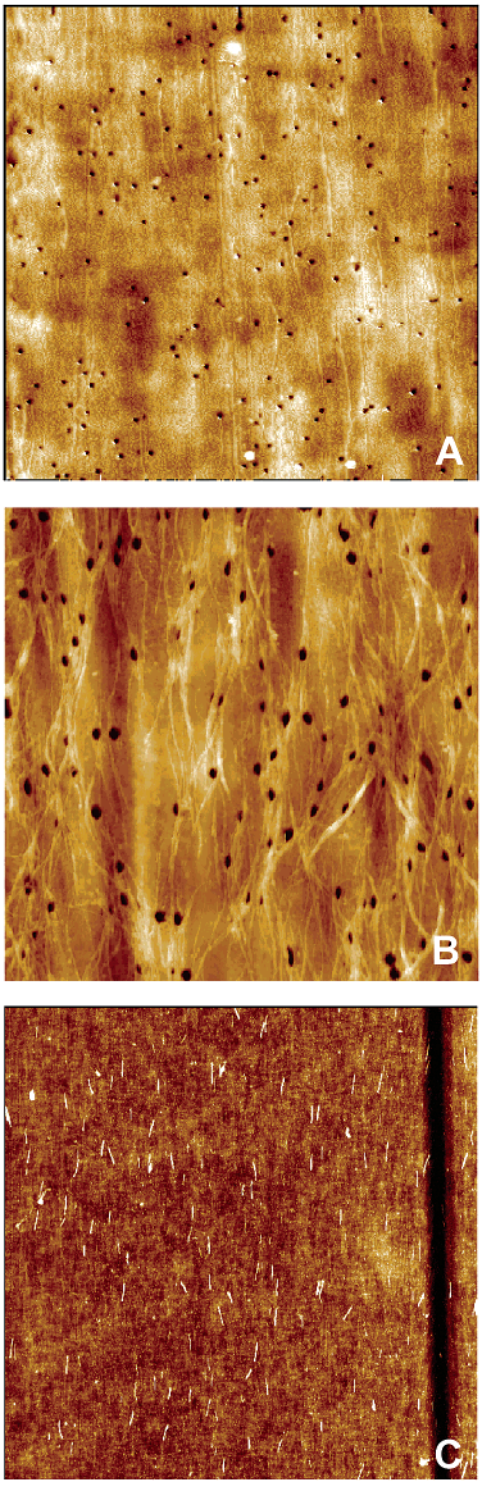

Figure 2. Oriented CNT films. CNTs deposited onto grooved polycarbonate membranes from LC solvents undergo spontaneous orientational ordering, as shown in these AFM images. In all cases the grooves were oriented vertically. Parts (a) and (b) show SWCNTs from E7 at low and high coverage. Dark spots are 100 or 200 nm diameter holes in the polycarbonate membrane through which the LC drains, leaving a thin film of CNTs. Both images measure 5×5 μm. (c) MWCNTs from 5CB (50×50 μm).

phase by holding the LC and substrate at 70 ± 5 °C during deposition. These showed no order at all ($S = 0.07 \pm 0.06$ based on 448 measurements from four samples), demonstrat-

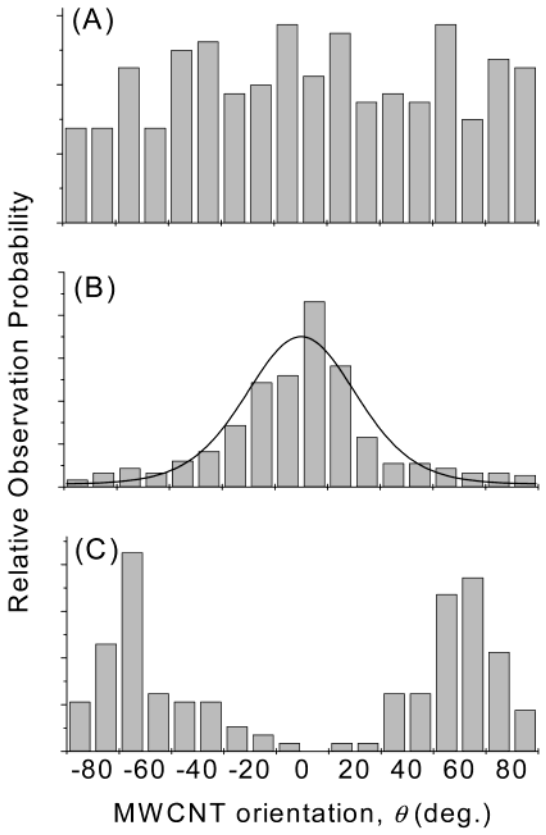

Figure 3. Quantification of long-range orientational order. The histograms show orientational distributions of MWCNTs in films prepared from suspensions of the LC 5CB by three different methods. The angle θ is the difference between the long axis of the CNTs and the average direction of substrate grooves. (a) Films prepared above the isotropic transition temperature of 5CB, where the LC behaves as a conventional liquid, show only random orientation (300 observations). (b) When deposited at room temperature, near the center of 5CB's nematic range, the LC director and CNTs align parallel to substrate grooves (361 observations). The solid line is a fit using the theory described in the text. (c) When deposition is performed in a magnetic field oriented in the substrate plane perpendicular to the grooves, the two alignment influences compete, leading to a bimodal distribution of alignment angles (160 observations).

ing that CNT alignment results from orientational coupling to the nematic matrix, and not from flow or capillary forces.

In addition to grooved surfaces, magnetic and electric fields can also be used to align LCs, and hence to control order in CNT films. The field can be applied parallel to the grooves, further improving overall uniaxial alignment, or alternatively used to produce more complex patterns by applying the field in the plane of the film along a direction different from the substrate grooves. This causes the two alignment influences to compete and the LC director and CNTs to adopt intermediate orientations.[14] We prepared MWCNT films in this way using a 1.3 T magnetic field oriented in the substrate plane, and perpendicular to the grooves. This led to a bistable alignment pattern with two symmetric degenerate orientations. The histogram in Figure 3c summarizes the alignment properties, which show two CNT populations oriented at $\theta = \pm 70°$ with respect to the substrate grooves for this set of conditions. The angle

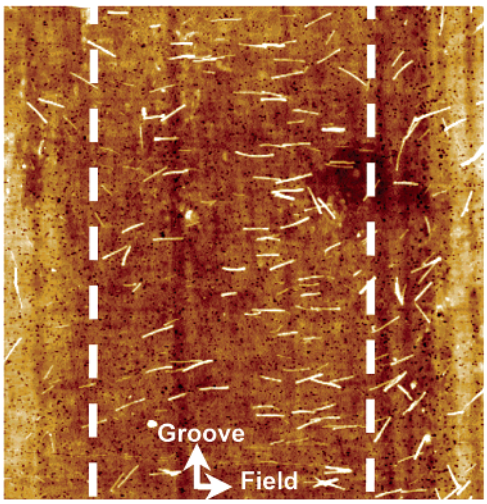

Figure 4. Electric field induced alignment. Microscopic patterning of CNT alignment can be achieved using local electric fields and LCs. This AFM image shows oriented MWCNTs deposited from 5CB in a 20 μm channel defined by two copper electrodes whose boundaries are indicated by dashed lines. A 1.8 V μm^{-1} electric field was strong enough to overwhelm the orientational influence of the grooves, which were perpendicular to the electric field in the channel. Similar results were obtained for SWCNTs.

depends on several factors including field strength, which can be varied to control the properties of the distribution.[15]

Alignment control with electric fields is an attractive strategy to enable micropatterning of CNTs and other nanoparticles for integration into complex device architectures. Here we demonstrate a simple procedure for connecting pairs of metal electrodes with CNT wires guided by LCs. Two 50 nm thick copper pads were evaporated onto polycarbonate membranes separated by a 20 μm wide channel, and a droplet of LC−CNT suspension was placed over the gap. As the fluid drained through the membrane, an electric field was applied between the contacts through a series capacitor, which limited the current flow. For fields larger than about 1.8 V μm^{-1}, the orienting influence overwhelmed that of the grooves, resulting in alignment of the LC director and CNTs parallel to the field, across the gap. Both SWCNTs and MWCNTs could be organized in this manner. An AFM image of a MWCNT film is presented in Figure 4.

Although the gap was longer than any single particle, at sufficiently high coverage SWCNTs overlapped to form a continuous network, establishing connections between electrodes. By counting the number of bridging SWCNTs in AFM images and measuring the resistance of the connecting films, the bulk resistivity parallel to the long tube axis was estimated to be $\rho_{||} = 10^1 - 10^2$ mΩ cm at room temperature. This range, which is slightly higher than previous reports for SWCNTs[16] ($\rho_{||} = 10^{-2} - 10^1$ mΩ cm), represents an upper limit since the calculation assumes every CNT participates in conduction and neglects the contact resistance of CNT junctions.

The effect of CNTs dispersed in 5CB on birefringence and the threshold voltage for the Freedericks transition were studied by Harte, who found evidence of particle alignment

in solution.[17] However, neither the degree of order nor the CNT orientation(s) were determined. Bulk LC alignment of anisometric particles has been studied most intensively in the context of ferronematic fluids, which are solutions of small magnetic particles in nematic solvents.[18,20,21] In such systems the particles dramatically amplify the response of the LC to weak magnetic fields.[19] Both parallel and perpendicular particle alignment have been observed, the preferred angle depending on particle size and the nature of LC adsorption to the particle surface. Theoretical treatments based on continuum theories of LC curvature elasticity lead to the prediction[20,21] that if LC molecules adsorb (or "anchor") parallel to the particle's long axis, parallel orientation always results. However if adsorption is tangential or radial, the particle's orientation will depend on its radius R, the anchoring strength W, and the LC elastic modulus K according to the unitless ratio $A = WR/K$. When $A \gg 1$, the particle orients parallel to the director, otherwise orientation is perpendicular.

This allows one to deduce that anchoring is parallel to the long axis of MWCNTs in 5CB and E7. Using values typical for nematics ($W = 10^{-6}$ Jm^{-2}, $K = 1$ pN) and $R =$ 10 nm, one finds $A \ll 1$, which would result in perpendicular particle orientation if anchoring was not parallel. The AFM images clearly show that the preferred MWCNT orientation is parallel to the nematic director. In practical terms, the theory suggests an additional way to rationally tune the orientational behavior of a particle (by adjusting W through its surface chemistry), opening the door to more sophisticated assembly strategies and to understanding and predicting alignment in systems of other mesoscopic particles. We note that a variety of methods now exist for functionalizing CNT surfaces.[22]

A rough estimate of the CNT alignment energy can be made from analysis of the probability distribution in Figure 3B. Burylov and Raikher have proposed a simple form for the orientational dependence of the free energy F of elongated particles in a nematic[23]:

$$F = F_{\parallel} + (F_{\parallel} - F_{\perp})\cos^2\theta$$

where $F_{\parallel}$ and $F_{\perp}$ are the free energies of parallel and perpendicular alignment. The probability of observing a particle oriented at an angle θ with respect to the global director is then

$$P(\theta) = Q^{-1}\exp(-F/kT)$$

where $Q = \int_{-\pi/2}^{\pi/2} \exp(-F/kT)$, k is Boltzmann's constant, and T is temperature. A variational fit to the data in Figure 3B (solid line) gives $F_{\parallel} - F_{\perp} \approx -3.8kT$, demonstrating that the alignment energy is very large. The actual difference is probably somewhat higher, because in addition to the finite alignment energy, the distribution is broadened by measurement error and imperfect LC alignment, which this calculation does not take into account.

It is unlikely that alignment of particles as small as SWCNTs can be understood in terms of the same anchoring mechanism discussed above—which ignores molecular-scale details by treating the fluid as a continuum—because their diameters are comparable to the size of individual LC molecules (1−2 nm). For particles as small as SWCNTs, a theoretical treatment taking into account specific intermolecular interactions and entropic ordering effects as in ref 24 is likely to prove more appropriate.

In summary, we report a variety of methods for post-synthesis organization of SWCNTs and MWCNTs under mild conditions using LC media. Both short- and long-range order are controlled in submonolayer-to-multilayer films, extending from micron to centimeter length scales. LC-induced alignment should be applicable to other anisometric nanoparticles, because objects with less than T_d symmetry generally undergo partial orientational ordering in a nematic medium.[25,26] An important advantage of LC solvents is that the external alignment force (magnetic or electric field, substrate grooves, etc.) need not exert any direct influence on the building block at all; the external influence aligns the LC, which in turn aligns the building blocks. There are more than 70 000 thermotropic LC compounds known, spanning a wide range of chemical properties and transition temperatures, thus ensuring compatibility with most solutes.[27]

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References

(1) Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. *Nature* **1996**, *382*, 607.
(2) van Blaaderen, A.; Ruel, R.; Wiltzius, P. *Nature* **1996**, *385*, 321.
(3) Caruso, F.; Caruso, R.; Möhwald, H. *Science* **1998**, *282*, 1111. Douglas, T.; Young, M. *Nature* **1998**, *393*, 152.
(4) Huang, Y.; Duan, X.; Wei, Q.; Lieber, C. M. *Science* **2001**, *291*, 630. Dirix, Y.; Bastiaansen, C.; Caseri, W.; Smith, P. *Adv. Mater*. **1999**, *11*, 223.
(5) Duan, X.; Huang, Y.; Cui, Y.; Wang, J.; Lieber, C. M. *Nature* **2001**, *409*, 66.
(6) *Science of Fullerene and Carbon Nanotubes*; Dresselhaus, M. S., Dresselhaus, G., Eklund, P. C., Eds.; Academic Press: San Diego, 1996.
(7) Zhang, Y.; Chang, A.; Cao, J.; Wang, Q.; Kim, W.; Li, Y.; Morris, N.; Yenilmez, E.; Kong, J.; Dai, H. *Appl. Phys. Lett*. **2001**, *79*, 3155.
(8) Ren, Z. F.; Huang, Z. P.; Xu, J. W.; Wang, J. H.; Bush, P.; Siegal, M. P.; Provencio, P. N. *Science* **1998**, *282*, 1105.
(9) Terrones, M.; Grobert, N.; Olivares, J.; Zhang, J. P.; Terrones, H.; Kordatos, K.; Hsu, W. K.; Hare, J. P.; Townsend, P. D.; Prassides, K.; Cheetham, A. K.; Kroto, H. W.; Walton, D. R. M. *Nature* **1997**, *388*, 52.
(10) Diehl, M. R.; Yaliraki, S. N.; Beckman, R. A.; Barahona, M.; Heath, J. R. *Angew. Chem., Int. Ed*. **2002**, *41*, 353. Bae, D. J.; Kim, K. S.; Park, Y. S.; Suh, E. K.; An, K. H.; Moon, J.-M.; Lim, S. C.; Park, S. H.; Jeong, Y. H.; Lee, Y. H. *Phys. Rev. B*, **2001**, *64*, 233401. Hertel, T.; Martel, R.; Avouris, Ph. *J. Phys. Chem. B* **1998**, *102*, 910.
(11) Smith, B. W.; Benes, Z.; Luzzi, D. E.; Fischer, J. E.; Walters, D. A.; Casavant, M. J.; Schmidt, J.; Smalley, R. E. *Appl. Phys. Lett*. **2000**, *77*, 663.
(12) SWCNTs were made using the HiPCO process of Nikolaev, P.; Bronikowski, M. J.; Bradley, R. K.; Rohmund, F.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *Chem. Phys. Lett*. **1999**, *313*, 91 and purchased from Carbon Nanotechnologies Inc., Houston, TX. MWCNTs were donated by Nanolab Inc., Watertown, MA, as

uniform films grown on catalyst-coated silicon substrates according to a procedure similar to that described in ref 8. MWCNTs were shaved from the substrate with a Teflon blade to give a monodisperse powder (CNT length 1.5−2.0 μm) and mixed with LC. Suspensions were prepared with a CNT/LC mass ratio of ∼1:1000.
(13) Merck kGaA, Darmstaft, Germany.
(14) A strong enough magnetic field can also orient CNTs by itself, as in ref 11.
(15) *The Physics of Liquid Crystals*, 2nd ed.; de Gennes, P. G, Prost, J., Eds.; Clarendon Press: Oxford, 1993.
(16) de Heer, W. A.; Bacsa, W.; Gerfin, T.; Humphrey Baker, R.; Forro, L.; Ugarte, D. *Science* **1995**, *268*, 845. Fischer, J. E.; Dai, H.; Thess, A.; Lee, R.; Hanjani, N. M.; Dehaas, D. L.; Smalley, R. E. *Phys. Rev. B* **1997**, *55*, 4921.
(17) Harte, A. *Caltech J. Undergrad. Res*. November, 2001.
(18) Chen, S.-H.; Amer, N. M. *Phys. Rev. Lett.* **1983**, *51*, 2298.
(19) Motoc, C.; Petrescu, E. *Mod. Phys. Lett.* **1998**, *12*, 529.
(20) Burylov, S. V.; Raiker, Y. L. *Phys. Lett. A* **1990**, *149*, 279.
(21) Brochard, F.; de Gennes, P. G. *J. Phys.*, **1970**, *31*, 691.
(22) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95. Star, A.; Stoddart, J. F.; Steuerman, D.; Diehl, M.; Boukai, A.; Wong, E. W.; Yang, X.; Chung, S.-W.; Choi, H.; Heath, J. R. *Angew. Chem.* **2001**, *113*, 1721.
(23) Burylov, S. V.; Raikher, Y. L. *Phys. Rev. E* **1994**, *50*, 358.
(24) Polson, J. M.; Burnell, E. E. *Phys. Rev. E* **1997**, *55*, 4321.
(25) Ivashchenko, A. V.; Rumyantsev, V. G. *Mol. Cryst. Liq. Cryst*. **1987**, *150A*, 1.
(26) *NMR Spectroscopy Using Liquid Crystal Solvents*; Emsley, J. W.; Lindon, J. C., Eds.; Pergamon: Oxford, 1975.
(27) Vill, V.; Sajus, H.; Thiemann, T. *Proc. SPIE* **1998**, *3318*, 160.

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