

Interactions of carbon nanotubes in a nematic liquid crystal. II. Experiment

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Multiwall carbon nanotube (CNT) colloids with different anchoring conditions are dispersed in pentyl-cyanobiphenyl (5CB), a thermotropic liquid crystal (LC) that exhibits a room-temperature nematic phase. The experiments make use of CNTs treated for strong planar, homeotropic, or Janus anchorings. Observations with a polarizing microscope show that the CNTs placed in a uniform nematic field stabilize parallel or perpendicular to \mathbf{n} depending on their anchoring conditions. In the presence of a splay-bend disclination line, they are first attracted toward it and ultimately, they get trapped on it. Their orientation relative to the line is then found to be parallel or perpendicular to it, again depending on the anchoring conditions. When a sufficient number of particles are deposited on a disclination line, they form a micro- or nanonecklace in the shape of a thin thread or of a bottle brush, with the CNTs being oriented parallel or perpendicular to the disclination line according to the anchoring treatment. The system exhibits a rich versatility, even if until now the weak anchorings appear to be difficult to control. In a next step, the necklaces may be glued by means of pyrrole electropolymerization. In this manner, we realize a true materialization of the disclination lines, and we obtain nanowires capable of conducting the electricity in the place of the initial disclinations that just worked as templates. The advantage of the method is that it finally provides nanowires that are automatically connected to predesignated three-dimensional (3D) electrodes. Such a 3D nanowiring could have important applications, as it could allow one to develop electronic circuits in the third dimension. They could thus help with increasing the transistor density per surface unit, although downsizing of integrated circuits will soon be limited to atomic sizes or so. In other words, the predicted limitation to Moore's law could be avoided. For the moment, the nanowires that we obtain are not completely satisfactory, particularly because they are thickened by aggregates in some places. However, the method is far from being optimized. A few electric charges deposited on the CNTs could remedy those aggregates.

DOI: [10.1103/PhysRevE.93.042703](https://doi.org/10.1103/PhysRevE.93.042703)**I. INTRODUCTION**

Carbon nanotubes (CNTs) [1] and liquid crystals (LCs) [2] are smart materials that both exhibit fascinating properties. They already provide useful applications, and they are promising for many others. The idea to associate them together naturally came in different laboratories. In the simplest case, nude CNTs are directly dispersed in the bulk of thermotropic nematic LCs. Experimentally, a simple mechanical action such as sonication for several hours is sufficient to realize a good dispersion [3,4]. This effect is not really surprising in itself, since the thermotropic LC molecules are known to be amphiphilic—in the etymologic and original meaning that the molecule likes two different types of chemical functions, here the alkyl and the phenylic ones—and therefore known to be an excellent solvent. Here, the attraction between LC molecules and CNTs is relevant to the π - π electron stacking that they can establish when in contact parallel to one another. Indeed, gentle stirring may give “surprisingly good results” too, and allows one to avoid sonication and its breaking effects on the CNTs [5]. Under these conditions, however, the concentration of the CNTs has to be very low, on the order of 0.005 wt %, for the suspension to remain below the coalescence threshold [4]. Interestingly, CNTs dispersed in a nematic media have been observed to orient parallel to the nematic director [6]. Similar observations have also been performed in chiral smectics that

exhibit ferroelectric properties [7]. Nevertheless, aggregates of CNTs are generally observed to form after a few hours, which indicates that the dispersions of nude CNTs are unstable indeed. To overcome this difficulty, it is possible to use a surfactant which may be physically adsorbed onto the CNTs. The risk is then that the surfactant molecules may desorb after a while and dissolve into the LC bulk. The CNT surface would then be left bare and again, nothing would prevent the CNTs from aggregating, and worse, at the same time, the process would unfortunately bring some pollution to the LC bath. This explains why experimentalists have developed chemical coatings for the CNTs. Different chemical functionalizations of the CNT surface have been tried, and this constitutes a second category of experiments [8,9]. The grafting of chemical functions on the CNT surface generally favors the interactions with resembling organic solvents since as detailed in Ref. [10], the van der Waals and London interactions are essentially attractive between similar chemical orbitals. This suggests that a coating of the CNTs with LC molecules bonded to them by covalent bonds should give good results, and indeed, high solubilities are obtained in this manner [11], up to concentrations of 5 wt % [12]. Chemical bondings of LC molecules are not the only way to coat CNTs. Good solubilities are also obtained on wrapping LC polymers around the CNTs [13].

Of particular interest is the case where a small amount of magnetic, iron or iron oxide, nanoparticles are attached to the external CNT surface. This surface modification not only favors the CNT dispersion in the nematic LC bulk, but the

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grafting of magnetic particles gives them magnetic properties too. The CNTs then become particularly sensitive to weak magnetic fields. With the coupling evoked above between the CNTs and the nematic director, the whole system now exhibits excellent orientational properties when submitted to small magnetic fields [14,15], a magnetic property obtained a long time ago with iron needles dispersed in lyotropic liquid crystals [16], and which has been particularly useful for experimental studies of the biaxial nematics [17]. Clearly, such suspensions correspond well to the ferronematic predicted a long time ago [18]. Let us also mention another interesting case where the carbon nanotubes are filled inside with α -Fe before being dispersed in pentyl-cyanobiphenyl (5CB), a LC whose major benefit is to exhibit a room-temperature nematic phase [19]. Other interesting physical properties have been evidenced in CNT dispersions in LCs. As the CNTs conduct electricity, a conduction regime may be observed above a percolation threshold where the CNTs are numerous enough for building up continuous paths from one electrode to the other [20]. Also, the good electronic conduction along the CNT axis increases the anisotropy of the electric properties in CNT dispersions. A consequence is their large dielectric anisotropy [13,21], which allows one to realize faster and more contrasted displays essentially because of the enhancements of the dielectric anisotropy [22,23] and of the K_{11} elastic constant [24].

Let us finally mention that the dispersion of CNTs is not limited to thermotropics. The CNTs may also be introduced in lyotropic systems. An elegant means to disperse the CNTs in lyotropic liquid crystals [25] makes use of the wrapping of single-stranded DNA molecules around the CNTs [26], a process that has been convincingly simulated with molecular dynamics [27]. More simply, the CNTs may be dispersed in water by means of bile salts [28]. In this manner, one may obtain a liquid crystal phase exhibiting a large anisotropy of conductivity [29].

In this paper, we present experiments on the interactions with two types of objects that the CNTs may undergo in nematic LCs. We focus on the interactions that they develop with the nematic field itself. More exactly, we study the preferred orientations that the CNTs choose in the field of the nematic director \mathbf{n} according to the anchoring conditions on their surface. We also examine the interactions of CNTs with splay-bend disclination lines. Both experimental behaviors are compared to the theoretical results published in Ref. [30]. We then discuss the possible use of these properties for materializing disclination lines. The process needs several steps. First, the CNTs slowly move toward the disclination lines, when the interaction is attractive, and eventually settle on them. After a sufficient number of CNTs have been attracted similarly, the disclination lines get materialized in the form of micronecklaces that further may be glued and converted into self-connected wires, as has recently been shown with glass particles [31,32]. Clearly, cylindrical objects such as the CNTs are more adapted than spherical particles to the symmetry of the wire that we intend to build. They should therefore produce mechanically more resistant nanowires that moreover would oppose a reduced drag to LC flows. We could then remove the 5CB bath by gently washing them with a solvent rinse, e.g., with ethanol, with the effect of suppressing the templates

used for their synthesis. We should thus be left only with nanowires directly connected to predesigned spots in the 3D space. The process could be used to connect integrated circuits in 3D automatically. This access to the third dimension could provide a way to extend Moore's law that predicts a continuous increase of the transistor density and that is essentially based on the downsizing of the connections between them. It would thus be possible to avoid the predicted limitation to this law that intrinsically arises from the limited size of the atoms, but indeed begins much before.

II. CNT ORIENTATIONS FOR DIFFERENT ANCHORING TREATMENTS

We try two types of multiwall CNTs. The smaller ones have a radius $R = 30$ nm and a length $L = 1-5$ μ m, and they are bought from Nanolab. The larger multiwall CNTs, with sizes $R = 70 \pm 25$ nm and $L = 5-7$ μ m, come from MER Corporation. The advantage of this last group of CNTs is that being larger, they are easier to observe with a polarizing microscope. The observation of CNTs is indeed not simple because their width is below the optical resolution of the optical microscope, and because, when they are dispersed in a nematic LC, the thermodynamic fluctuations of \mathbf{n} blur the images. However, the introduction of the CNTs in a nematic LC has a positive effect that helps with observing them. Because the CNTs interact with the director field around \mathbf{n} by means of their anchoring properties, they produce a distortion of the nematic phase that extends a few micrometers away. Due to nematic birefringence, the distortion is strongly coupled to the light, which makes the CNTs more easily visible. Surprisingly, the CNTs may also be observed when dispersed in the isotropic phase a few degrees above the nematic phase transition. In this case, we suspect that a thin layer of nematic phase is induced from the CNT surface as LC phases often do on isotropic interfaces, e.g., see Ref. [33], and that then a birefringence shell forms around the CNT. This shell is naturally larger than the CNT width itself and may therefore come inside the resolution limits of current polarizing microscopes. However, this is not a necessary condition as, in black field illumination, tiny objects may be observed even below the optical resolution, just as stars are visible to the naked eye. Similarly, the light that arises from birefringence objects, and which cannot be extinguished with crossed polarizers, can easily be detected in black field. Analogous behaviors have also been observed with silica spheres dispersed in the isotropic phase of a nematic liquid crystal. Due to thermal fluctuations, the particles and their surrounding nematic shells undergo rotational diffusion. Being uniaxial and observed between crossed polarizers, these shells thus exhibit stochastic changes of light intensity, which give them the spectacular appearance of twinkling stars [31].

A. CNT dispersion

First, the CNTs have to be dispersed in the 5CB nematic LC. Different means may be used to avoid their aggregation. A first idea consists of using surfactants. They deposit on the CNT surface, provided that they interact stronger with the CNTs than with the LC molecules. Such a surface treatment is sometimes referred to in terms of wetting properties [10].

The surfactants are thus grafted on the CNT surface by means of (physical) van der Waals interactions or (chemical) oxidation reactions. In some cases, polymers such as gum arabic, or DNA molecules, may wrap around them. Their role is to prevent the CNTs from coming into contact with one another and thus to develop strong London interactions that would aggregate them. However, in the same way, these surfactants could prevent the electric conduction between the CNTs when forming a necklace on a disclination line. This consequence could preclude them from being used for making thin self-connected wires [31,32]. The conductivity between CNTs in contact with one another therefore has to be carefully tested in cases where a surfactant is used. If this test fails, and no appropriate surfactant seems available, another possibility could be to deposit electric charges of the same sign on the CNTs in order that they repel from one another by means of Coulomb force. This is possible if the electropositivity (or electronegativity) of the CNTs is sufficiently different from that of the LC molecules. Such a property may be obtained on grafting a few acid, or basic, chemical functions on them. This would provide a repulsive Coulomb force, capable of stabilizing the dispersion. Such graftings do not need to be numerous to provide a few electric charges to each CNT. The repulsive force that results should, however, be weak enough not to prevent the frank contact between neighboring CNTs trapped on a disclination line, which is necessary for the final nanowire to conduct electricity. If, however, these methods based on surface treatments of the CNTs do not work, a last solution could simply be to reduce the number density of the particles. Then, the segregation is not formally forbidden but is reduced and delayed so much that it cannot occur during the effective experimental time.

Experimentally, the most efficient protocol that we use to disperse nude CNTs in a 5CB LC consists first in dispersing the CNTs in dichloromethane (CH_2Cl_2) and then in introducing the mixture in the nematic. The solvent is then evaporated by heating the mixture up to 80°C . As the nude CNTs bear no electric charges, they do not repel electrostatically, and when they are at short distance, they attract one another by means of a strong London interaction between their benzene rings (Sec. I). However, the dispersion may stay stable for a long enough time to let us study the CNT condensation on disclination lines. The probability that the CNTs meet together has to be weak, and indeed we observe that if the CNT density does not much exceed 5000 per mm^2 , the formation of aggregates could be neglected for hours, which is sufficient for performing the experiments discussed below. In this simple approach, we therefore do not really need to improve the stability of the dispersion, for instance, when using the methods discussed above.

We may now study in which direction the dispersed CNTs point to, relative to the nematic director \mathbf{n} , or to the disclination line direction if they are caught on it. Naturally, the result will depend on the anchoring properties of the CNTs.

B. Planar anchoring

Observations of large CNTs dispersed in a nematic LC are performed with a polarizing microscope in a uniformly oriented cell or in the vicinity of a vertical splay-bend

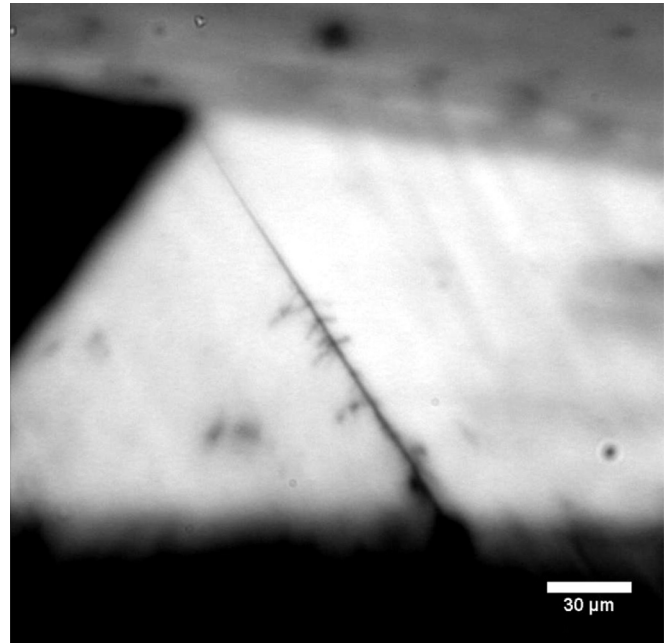


FIG. 1. Splay-bend disclination line joining pre-designed spots on opposite glass plates. CNTs with planar anchoring begin to condense perpendicularly on a disclination, forming an object in the shape of a bottle brush. The different gray colors correspond to the different rubbing directions that are necessary on the two plates of a sample to force a splay-bend disclination line in it (see Ref. [32]). The spacing distance between the two glass plates is about $140\ \mu\text{m}$. They are shifted by about the same distance in order to make the line more easily visible. The focus is on the CNTs about one-third of the distance from the upper plate.

disclination line, namely, in places where the orientation of \mathbf{n} is well known. They clearly show that the nude CNTs systematically orient parallel to \mathbf{n} . Such a CNT orientation is consistent with the strong London interaction between the phenyl rings of both the CNTs and the LC molecules that makes them stick tangentially to the CNTs [21]. This property explains the planar anchoring of the nude CNTs [30]. Interestingly, the CNTs then exhibit an orientational order parameter between 0.6 and 0.9, depending on the experimental conditions, which is somewhat larger than the natural order parameter of the nematic host that generally ranges close to 0.6 [34].

The experimental study of the interaction of a CNT with a splay-bend disclination line, first needs one to prepare a line at a pre-designed place upon treating the plates of a sample with appropriate conflicting conditions of planar anchoring. In a second step, the disclination line is tilted by slightly shifting the upper plate from the lower plate while keeping the spacing distance constant in order to make the observation easier [31]. The CNTs are thus observed to condense on the disclination line and to sit perpendicularly to it. Unfortunately, we do not observe the formation of a ribbon but of a kind of bottle brush (Fig. 1). This observation is consistent with the scenario proposed in Sec. III A of Ref. [30] that the CNTs definitely stick to one another at their first contact. This mechanism thus prevents any further reorientation of the CNTs in the same plane, in particular, in the symmetry plane of the splay-bend

disclination line, which would be necessary for producing a ribbon.

C. Homeotropic anchoring

In order to imprint a homeotropic anchoring onto the CNTs, we completely functionalize their surface with aliphatic chains. A two-step process is used. First, the CNTs are oxidized under the action of a concentrate mixture of nitric and sulphuric acids submitted to intense sonication. In this manner, various oxygen-containing groups are grafted onto the CNT surface, mainly carboxyl groups [35]. The sonication process also cuts long CNTs in pieces and opens up their caps [36]. In a second step, the CNTs are extracted and then dispersed in a distilled water solution of octadecyltrimethoxysilane (ODTS) (0.1 wt %). Thus, long-chain silane molecules connect onto carboxyl groups via ionic attachments [37] so that the CNTs are finally coated with aliphatic chains. They are known to provide strong homeotropic anchoring properties to the substrates that they cover because of the preferential London interaction that they exert with the aliphatic tips of the thermotropic LC molecules. Another advantage of such a coating is that it helps with dispersing the CNTs into the 5CB LC, more because of the large entropic cost of the chain interpenetration in their respective furs than because the London interactions between aliphatic coatings are smaller than the interactions between bare CNTs.

Observations performed in the same conditions as in the planar anchoring case show that the homeotropic CNTs orient parallel to the nematic director \mathbf{n} , that is, in the same way as in the planar case. This is consistent with the calculations of the coupling between a CNT and the director \mathbf{n} performed in the strong anchoring case in Ref. [30] (see Sec. II B). Interestingly, we do not observe CNTs perpendicular to the nematic director \mathbf{n} . This would correspond to a weak anchoring, but as discussed in Refs. [30] and [38], the weak anchorings should not be experimentally stable, as large impurity molecules initially solved in the nematic LC should progressively settle on the substrate and modify its anchoring properties. This probably explains why we do not observe the perpendicular orientation with homeotropic CNTs deposited on disclination lines.

The CNTs with strong homeotropic anchoring are readily attracted toward the disclination lines, generally after a non-rectilinear trajectory, as in the planar anchoring case [39]. They ultimately get trapped onto them, forming micronecklaces of CNTs. This demonstrates that the interaction of homeotropic CNTs with a disclination line is rather strong, which is consistent with our estimate of the coupling energy between them (Eq. (13) in Ref. [30]). In order to make the disclination line and the micronecklace of CNTs more visible, we proceed as in the planar case. We shift the upper plate by a distance on the order of the sample spacing (Fig. 2). However, for this photograph we have performed a larger shift than in the planar case (Fig. 1), so that we now observe that the disclination line gets partially projected on the plate instead of just being tilted. This projection onto the substrate explains why the focus stays the same all over the photograph, conversely to Fig. 1. Such a projection results from the lower energy cost of surface disclination lines compared to bulk ones. As

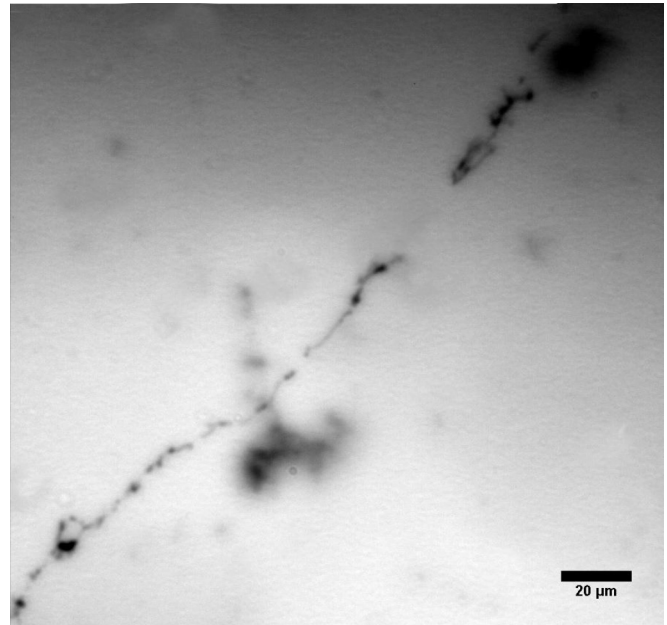


FIG. 2. CNT necklace in the isotropic phase projected on a glass substrate and stabilized by CNT-substrate nematic bridges.

discussed in Ref. [32], the projection occurs if the shift exceeds a threshold distance that depends on the ratio of their respective energies per unit length. A direct consequence of the projection is that the total length of the disclination line is suddenly increased so that the CNT micronecklace breaks in several places.

The CNTs are indeed difficult to observe when immersed in the nematic phase, because they are small and because the visibility is poor in thick nematic samples due to the light scattered from the \mathbf{n} fluctuations. In order to improve the visibility, we heat up the samples into the isotropic phase. Interestingly, the micronecklace survives such a heating, although the nematic force at the origin of the micronecklace cohesion has then vanished and though the transition front from the nematic to the isotropic phase is known to interact strongly with the colloid particles and to be able to push them away. In particular, such a property of pushing particles by means of a phase transition front has previously been used to gather particles and therefore to build micronecklaces [31]. Clearly, the CNTs resist dispersion here because they somehow adhere to the substrate partly by means of van der Waals interactions and partly also because of nematic bridges that arise in the narrow spaces between solids immersed in the isotropic phase, a property that may be understood if one recalls that the solid interfaces with the isotropic phase are indeed covered by a thin nematic shell that is directly induced by the surface field [33]. When in contact with one another in a micronecklace, the nematic shells of neighboring CNTs join together by means of capillary forces and therefore reinforce the micronecklace cohesion.

Both adhesion forces are of the same order of magnitude. The van der Waals adhesion force of a CNT on a glass substrate may be evaluated upon taking the derivative of the van der Waals interaction between two parallel cylinders, one of them

exhibiting an infinite diameter [10]:

$$F_{vdW} = \frac{AL}{8} \sqrt{\frac{3R}{2}} \frac{1}{D^{5/2}}, \quad (1)$$

where A is the CNT-glass Hamaker constant. As both materials have completely different polarizabilities on the whole range of frequencies, their London interaction is small. We thus may evaluate $A \sim 10^{-20}$ J [10], and $F_{vdW} \sim 3 \times 10^{-9}$ N, with $R \sim 30$ nm, $L \sim 1 \mu\text{m}$, and upon appreciating the distance of the CNT to the substrate, $D \sim 1$ nm.

The capillary force that the nematic bridge exerts between the CNT and the substrate is simply given by

$$F_{\text{cap}} = 2\gamma_{\text{NI}} L, \quad (2)$$

where γ_{NI} is the surface energy of the nematic-isotropic phase interface. Its value should be 1 order of magnitude smaller than the air-isotropic phase interface, so that we should have $\gamma_{\text{NI}} \sim 10^{-3}$ J m⁻² [40], and therefore, the capillary force that stabilizes the CNT on the substrate should be $F_{\text{cap}} \sim 2 \times 10^{-9}$ N, in the same range as the van der Waals force. This similarity between both forces is essentially due to the large diameter of the CNTs that we use here. With smaller ones, the capillary force will dominate.

D. Janus anchoring

Preparing CNTs with Janus anchoring is not so straightforward as treating CNTs for planar or homeotropic anchorings. It requires several steps. First, a low-concentration suspension of pristine CNTs in CH₂Cl₂ is spread over a glass plate in such a way that after evaporation the CNTs are individually dispersed on the plate. A 2-nm layer of titanium, which is known for its solid grip on graphene [41], is then evaporated on them, followed by a 10-nm layer of gold. As the CNTs have remained stuck on the substrate, only one side is covered with gold whereas the other side stays bare (Fig. 3). In a third step, the CNT supporting plate is immersed in a 2 wt % ethanol solution of dodecanethiol for 3 hours under continuous stirring. The substrate is finally washed with pure ethanol, and the

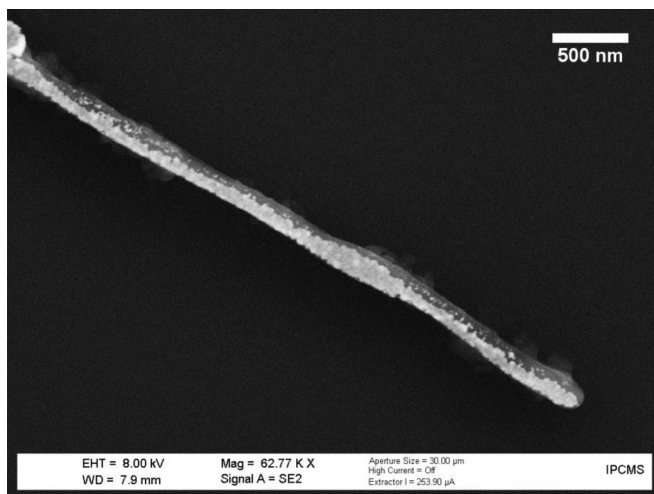


FIG. 3. SEM image of Janus CNT having one side coated with gold.

CNTs are detached from the substrate by means of sonication before being dispersed in the 5CB nematic LC.

We perform the experiments in the same conditions as previously in the planar and homeotropic anchoring cases, that is, with strong anchoring conditions, as discussed above. They show that the Janus CNTs now orient perpendicular to the nematic director \mathbf{n} instead of parallel to \mathbf{n} , which is consistent with the results of the discussion of Ref. [30] (see Sec. II C and Table I).

In a second set of experiments, the interaction of Janus CNTs with a splay-bend disclination line is studied. As in the cases of planar or homeotropic CNTs, the disclination is produced perpendicular to the sample at the designed places [32]. We observe that the Janus CNTs are attracted by the splay-bend disclination lines, similar to the CNTs previously treated for strong planar or homeotropic anchorings, and that they ultimately get trapped onto them. When they fix onto the disclination lines, they orient parallel to the lines in the same manner as the homeotropically treated CNTs (Sec. III C and Table I in Ref. [30]). So, in summary, the Janus CNTs do not exhibit a key advantage compared to the CNTs with a strong homeotropic anchoring. Since they are more difficult to obtain, in small batches only, we do not use them any longer for preparing nanonecklaces and we come back to the homeotropically treated CNTs.

III. SELF-ASSEMBLY OF A THIN NANONECKLACE ON A DISCLINATION LINE

It is tempting to use the CNT interaction properties, discussed above and in Ref. [30], to build thinner and stronger nanowires that exactly connect in three dimensions to pre-designed electrodes on facing substrates. The method that uses disclination lines as templates for the synthesis of nanowires has first been evidenced with spherical beads and seems to be most promising, as several disclinations may simultaneously be produced and connected at the desired places on substrates that have received an appropriate surface treatment [31,32]. Then the disclination lines attract the CNTs and eventually are materialized in the shape of thin nanonecklaces. Moreover, if the disclination lines have been designed to join electrodes, these nanonecklaces may further be fixed with an appropriate conducting glue to form nanowires. Practically, a small amount of pyrrole that is initially solved in the 5CB LC is gently polymerized by means of electropolymerization [32]. With this method the pyrrole radicals are directly produced on the nanoelectrodes that each bead of the necklace constitutes and they quickly condense on them, forming a polypyrrole seal that ultimately ties them together until elaborating a continuous nanowire [42]. In this manner, electric nano-connections are realized (Fig. 4). This process for gluing the particles on the necklace is facilitated if the particles are initially coated with a thin layer of polypyrrole before being dispersed in the 5CB nematic LC. The presence of pyrrole functions on the particles helps the polypyrrole production that is necessary to fix the necklace of CNTs along the disclination line. This polypyrrole coating has the double benefit of providing a strong homeotropic anchoring on the particle surface and to make it conductive of electricity. Such a conductive property is clearly necessary for the electropolymerization when using isolating

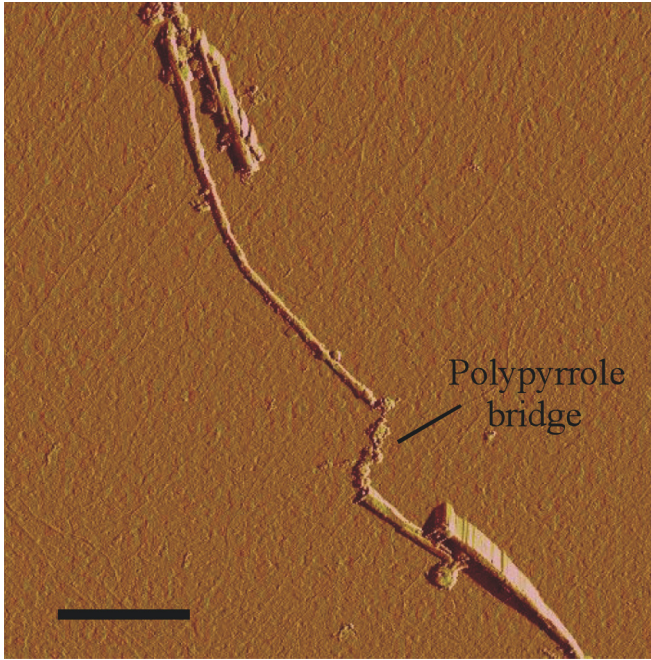


FIG. 4. AFM image of a polypyrrole bridge between two CNTs after the nanowire has been extracted from the sample, washed with alcohol, and dried. The bar is $3\ \mu\text{m}$ long. The maximum height of the object is $1\ \mu\text{m}$ from the substrate.

glass beads. Because the CNTs are already conductive, they do not really need an initial polypyrrole coating and we may as well coat them with a light cover of silane after a soft oxidation (Sec. II C). Such a treatment is easy to perform and is sufficient to disperse the CNTs in the 5CB LC and to give them the appropriate strong homeotropic anchoring. We therefore prefer to use it.

One may notice in Fig. 2 that the CNT necklace also contains small aggregates. They will naturally subsist in the subsequent nanowires after sticking by pyrrole electropolymerization. In order to avoid such aggregates, it would be possible to improve the dispersion of the CNTs in the 5CB LC. A method could be to load them with a few elementary electric charges, for instance, by performing a limited silane treatment after a few acid functions have been grafted at their surface.

In order to prove that a new structure has really been built up and therefore that the gluing process of a nanowire has been efficient, we have to suppress the template used to build it. This test just needs to heat up the nematic LC into the isotropic phase. The disclination line that served as a template then vanishes out. The observation that the nanowire survives the test is in principle sufficient to prove its reality [31]. At the same time, once in the isotropic phase, the fluctuations of the nematic director that usually blur the images in the nematic phase have disappeared. The visibility of the nanowire is then improved. To be even more demonstrative and in order to definitely show that the nanowire is no more dependent on the template that was used to create it, we may observe that it is able to sustain a gentle flow of the surrounding isotropic liquid. This method has also the advantage to discard the trivial case where the whole bulk has indistinctly been jellified [32].

Obviously, the CNTs with strong homeotropic and Janus anchorings, because they arrange parallel to the disclination lines, are well suited to realize thin necklaces and therefore, for building thin conducting threads. In particular, they allow one to realize much thinner wires than when using spherical particles [39]. The hydrodynamic drag that results in a LC flow is then subsequently reduced so that the CNT nanowires resist to larger flows before breaking up.

Though the presence of a LC bath around the nanowires should not *a priori* be a problem for practical applications of such a 3D wiring, we may now remove the 5CB LC upon slowly draining it away in the isotropic phase. However, at this stage, we may object that the interface of the isotropic 5CB with the air has a large surface tension that could break the wire anyway. Let us notice then that we may avoid this devastating impact of the 5CB surface tension by replacing it with a lower surface tension liquid such as ethanol before evaporating it away. The process could be realized continuously, as 5CB easily dissolves in alcohol.

IV. CONCLUSIONS

Using polarizing microscopy, we have analyzed the orientations that large CNTs take at equilibrium in a uniform nematic field or on a splay-bend disclination line, according to their anchoring treatment, namely, the planar, homeotropic, or Janus anchoring treatments. More exactly, the CNTs with a planar anchoring treatment are found to orient parallel to the nematic director \mathbf{n} and to stand perpendicular to the splay-bend disclination lines after they have been attracted onto them. However, they build a bottle-brush-like object instead of producing a regular ribbon because of the larger entropic cost [30]. These observations are consistent with the conclusions based on the estimates of the CNT coupling energies with the nematic field and with the disclination line, respectively [30].

The CNTs with homeotropic anchoring work differently. They indeed orient parallel to the nematic director \mathbf{n} such as the planar CNTs do, in agreement with the theoretical results, at least in the strong anchoring case since we lack of reproducible evidence in the weak anchoring case [30]. The CNTs then settle parallel to the splay-bend disclination lines after they have been attracted to them. Interestingly, the process is iterative and new CNTs may come and stick on the same disclination line. After a large number of CNTs have been attracted and collected on the line, we obtain a thin nanonecklace that moreover exhibits a slight conductivity. If the disclination line has been designed to join electrodes, we may glue the particles to one another on the necklace by means of pyrrole electropolymerization. This process ultimately leads to a complete materialization of the disclination line. In order to demonstrate that the materialization is effective, we may suppress the disclination line by melting the whole sample into the isotropic phase. A better proof may be obtained, however, on applying a small flow on the isotropic liquid in order to test the real solidity of the synthesized nanowire [31,32]. In summary, the method that we suggest employs the disclination lines of a nematic LC as templates to build nanowires connected to predesigned electrodes in the 3D space. In particular, these electrodes could belong to different integrated circuits, and the synthesized nanowires could directly connect them together. The process

seems to be most promising, and indeed, no other way is available to-date to realize such a goal. It could be a practical means to overcome the predicted limitation to the famous Moore's law on two-dimensional (2D) electronic density. Clearly, the use of elongated and conducting particles as CNTs is more appropriate to this aim than spherical silica beads as initially proposed. Being thinner, they should withstand larger flows during the LC evacuation. This property, which also needs a strong gluing quality between the CNTs, has to be quantitatively verified, too. The nanowires that we have obtained until now with the disclination-made templates are far from being optimized. More experiments are indeed necessary for improving again the quality of the synthesized wires. Special attention should be given to the residual CNT aggregates that we have noticed in Sec. II C. Methods are available to avoid them. The deposit of a few electric charges of the same sign on each CNT seems to be most promising.

The CNTs with Janus anchoring work at the opposite of the planar CNTs, at least in the strong anchoring case, since again

we have no reproducible access to the weak anchoring case. They orient perpendicular to the nematic director \mathbf{n} and they stand parallel to the disclination lines when they enter into contact with them. These observations are again consistent with the theoretical results of Ref. [30]. As they orient parallel to the disclination lines, they could be used as well to produce 3D self-connected nanowires. They are not really difficult to prepare in small quantities. However, though these nanowires are of good quality, it is not clear if they constitute a real improvement when compared to the nanowires made of simple homeotropic CNTs. So, in view of the promising behavior of the homeotropic CNTs, the CNTs with Janus treatment could remain only a curiosity.

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