Colloidal analogues of polymer chains, ribbons and 2D crystals employing orientations and interactions of nano-rods dispersed in a nematic liquid crystal

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Robust control over the position, orientation and self-assembly of nonspherical colloids facilitate the creation of new materials with complex architecture that are important from technological and fundamental perspectives. We study orientation, elastic interaction and co-assembly of surface functionalized silica nano-rods in thin films of nematic liquid crystal. With homeotropic boundary condition, the nano-rods are predominantly oriented perpendicular to the nematic director which is different than the mostly parallel orientation of the micro-rods. The percentage of perpendicular nano-rods are significantly larger than the parallel nano-rods. The perpendicular nano-rods create very weak elastic deformation and exhibit unusual, out-of-plane, attractive interaction. On the other hand, the nano-rods oriented parallel to the director create strong elastic deformation and shows anisotropic, in-plane, dipolar interaction. In both orientations, the induced defects reside in the nano-rods. With the help of a dynamic laser tweezers and using nano-rods as building blocks we demonstrate colloidal analogues of linear polymer chains, ribbons and two-dimensional binary crystals.

Achieving colloidal analogues of atoms, molecules and chemical elements has been challenging in colloidal science. In this field, significant advances have been made in variety of systems such as janus magnetic rods, DNA coated patchy colloids, co-assembly of soft patchy nanoparticles, paramagnetic colloids, photocatalic colloids etc1–9. Mostly they are dispersed in an isotropic medium like water and the interaction forces are short-range. When colloidal particles are dispersed in nematic liquid crystals they create strong elastic deformation in the director field denoted by a dimensionless unit vector, \( n \). The deformation often culminates in the form of topological defects in the vicinity of the colloids depending on the surface anchoring and the shape of the colloids11–16. The colloids interact anisotropically via long-range elastic forces which have no analogues in regular colloidal systems in an isotropic dispersive medium. The elastic forces in liquid crystal are usually dipolar or quadrupolar type akin to electrostatics. The interplay of defect and elastic interaction gives rise to complex colloidal structures and superstructures starting from one to three-dimensions17–21. The diversity in the structure is often introduced by varying the shape, size and genus of the colloids17,22–29.

In this paper, we report experimental studies on the dispersion of silica nano-rods in a nematic liquid crystal. We focus on the spontaneous orientation, elastic interaction and directed co-assembly with micro-rods and microspheres in a nematic liquid crystal. We find that the silica nano-rods are predominantly oriented orthogonal to the nematic director and exhibit out-of-plane attractive interaction. The induced defects reside in the nano-rods. Using dynamic laser tweezers we have designed various colloidal analogues of linear polymer chains, ribbons and two dimensional binary colloidal crystals. Ours is the first experiment among several nematic colloidal systems, showing spontaneous out-of-plane interaction giving rise to vertical assembly of silica nano-rods in a liquid crystal. Such studies have important bearing on the efforts in making three-dimensional, periodic nematic colloidal systems, in which the orientational direction of the nano-rods is orthogonal to the nematic director.

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Figure 1. (a) SEM image of silica rods of mean length and diameter are \( l = 3 \mu m \) and \( d = 200 \) nm respectively (designated as nano-rods). (b) CCD image of a few DMOAP coated silica nano-rods dispersed in a planar cell of 5CB liquid crystal, (c) Statistics of orientation of the nano-rods with respect to the director. Different colours correspond to different cell thicknesses namely, 2, 5 and 10 \( \mu m \) respectively. POM images with, (d) crossed polarisers, (e) an additional \( \lambda \)-plate (530 nm) inserted between the polarisers and sample. Schematic diagram of director distortions surrounding a nano-rod oriented, (f) parallel to the director, and (g) perpendicular to the director. (Inset) Cross-section of director distortion. Double headed arrow below \( n \) denotes the director. White cross denotes polariser and analyser.
The difference in the orientation behaviour of the silica nano and micro-rods can be understood based on a dimensionless parameter $p = W/RK$. If $p > 1$, the silica rods are oriented parallel and if $p < 1$ they are oriented perpendicular to the director. For a given $W$, the orientation mainly depends on the radius of the silica rod as $p \propto R$. The diameter of the nano-rods is almost 4 times smaller than that of the micro-rods, hence $p$ could be less than one and the perpendicular orientation of the majority of nano-rods is favourable. Also it has
been shown that for nano-rods with high aspect ratio the surface anchoring energy per rod can be written as
\[ F = \frac{\pi LDW}{4} (1 + \cos^2 \theta), \]
where \( D \) is the diameter and \( \theta \) is the angle between the director and the long axis of the nano-rod. This energy is minimised when they are perpendicular to the director i.e., \( \theta = \pm \pi/2 \).

In what follows, we study elastic pair interaction of nano-rods oriented both parallel and perpendicular to the director. Figure 3 presents the result of two interacting nano-rods oriented parallel to the director. Two nano-rods were kept apart at a distance with the help of the laser tweezers and allowed to interact freely. The centre to centre separation (\( R \)) was measured as a function of time and shown in Fig. 3(a). The time dependent separation corresponding to dipolar interaction is fitted to the equation\(^{32}\): \[ \alpha = -\frac{R(t)}{R_0(t)^5} \] with \( \alpha = 7.3 \times 10^3 \mu m^5/\text{sec} \) corresponding to dipolar interaction. Inset shows the interaction potential as a function of separation. Colour coded time trajectories (Relative coordinate) of two nano-rods oriented parallel to the director and situated at different angles with respect to the director when both the nano-rods having, (b) similar director orientation, (c) opposite director orientation (see the yellow and blue colours of the \( \lambda \)-plate images in two cases).

Figure 3. (a) Time dependent centre to centre separation (\( R \)) between a pair of collinear nano-rods parallel to the director (Movie S1)\(^{30}\). Red line shows the nonlinear least square fit to \( R(t) = (R_0^5 - 5\alpha t)^{1/5} \) with \( \alpha = 7.3 \times 10^3 \mu m^5/\text{sec} \) corresponding to dipolar interaction. Inset shows the interaction potential as a function of separation. Colour coded time trajectories (Relative coordinate) of two nano-rods oriented parallel to the director and situated at different angles with respect to the director when both the nano-rods having, (b) similar director orientation, (c) opposite director orientation (see the yellow and blue colours of the \( \lambda \)-plate images in two cases).

We study the elastic pair interaction of nano-rods oriented perpendicular to the director. A few representative CCD images taken at different times of two interacting nano-rods are shown in Fig. 4(a). It is observed that due to the attractive interaction one nano-rod goes under the other in the vertical direction (out-of-plane). The variation of interparticle separation (Fig. 4(b)) can be fitted to the equation\(^{32}\): \( R(t) = (R_0^5 - \alpha t)^{1/5} \), corresponding to the quadrupolar interaction. The variation of interaction potential is also shown in the inset. The relative coordinates of two interacting nano-rods show that the attractive interaction is short-range and does not depend on the approaching angle hence the interaction is isotropic (see Fig. 4(c)). A vertical ribbon-like structure is prepared by assembling
14 nano-rods and shown in Fig. 4(d). All the nano-rods can not be seen from the top because of vertical assembly. To visualise the ribbon properly and check the stability, the structure was tilted by dragging with the help of the laser tweezers. Simultaneously images were captured at different time intervals as shown in the subsequent images. Finally the structure relaxes back to the initial configuration when the laser is switched off. The interaction of spherical nanoparticles dispersed in nematic liquid crystals has been studied by Ryzhkova et al.24 and found to be always in the plane of the sample. Thus out-of-plane attractive isotropic interaction of nano-rods is unusual and potential for making hierarchical materials assembly.

We construct a variety of stable and linear colloidal structures employing the nano-rods. Figure 5(a,b) shows a long chain of ten nano-rods, which are oriented along the director. It appears as a continuous string like object without any discontinuity in-between. The linear chain of nano-rods is akin to a linear homopolymer in which each nano-rod resembles a monomer. A schematic director orientation surrounding the chain is shown in Fig. 5(c). In the similar way ten nano-rods were assembled side-by-side to form a horizontal ribbon-like structure as shown in Fig. 5(d,e). A schematic director orientation surrounding the ribbon is also shown in Fig. 5(f).

To construct co-assembled structures we used DMOAP coated microspheres and nano-rods. A dipolar microsphere of diameter 1 \( \mu \)m and a nano-rod oriented parallel to the director have attractive interaction and forms a match-stick like object (Fig. 6(a–c)). This helps to understand in which side of the nano-rod the point defect is hidden. For example, the \( \lambda \)-plate image (Fig. 6(b)) clearly suggests that the point defect is residing close to the right side of the nano-rod. When a quadrupolar microsphere is allowed to interact with the nano-rod, the result is very different. In this case, the Satrun ring defect of the microsphere becomes unstable as they approach to

Figure 4. (a) Sequence of CCD images of a pair of interacting nano-rods oriented perpendicular to the director. Nano-rods are attracted towards each other and one nano-rod goes below the other (Movie S2). (b) Time dependent centre to centre separation (R) of a pair of nano-rods. The red line shows nonlinear least square fit to \( R(t) = (R_0 - 7\alpha t)^{0.7} \) with \( \alpha = 2.4 \times 10^4 \mu \text{m}$/sec corresponding to quadrupolar interaction. Inset shows the variation of interaction potential with separation. (c) Colour coded time trajectory (Relative coordinate) of two nano-rods approaching each other at different angles with respect to the director. (d) Vertical ribbon-like structure made of fourteen nano-rods and temporal evolution of the structure when a gentle force was applied with the help of the optical tweezers.
each other and finally the quadrupolar microsphere is converted to a dipolar microsphere. A sequence of CCD images taken at different times of a 2.3 μm microsphere are shown in Fig. 6(d). The experiments were performed with varying diameter of the microspheres and found that beyond about 3.5 μm microsphere, the quadrupolar structure is stable and no transformation from quadrupole to dipolar is observed. For example, Fig. 6(e–g) shows a stable association when two nano-rods from the opposite directions were allowed to interact in the equatorial plane of a spherical colloid of diameter 5.2 μm. The interaction is attractive and the assembly as a whole looks like a snake charmer’s flute. If they approach from any other plane then they are attracted to the Saturn ring similar to the response of spherical nanoparticles.

Using different combination of nano-rods, micro-rods and microspheres, we prepared several linear chains as shown in Fig. 7. Figure 7(a) shows the optical photomicrograph of a linear chain of assembly of several 5.2 μm diameter dipolar colloids and nano-rods. The binding energy for pair interaction is approximately 4000 kBT. The colloids were arranged in an alternative fashion and the linear chain is parallel to the director. Corresponding images taken with λ-plate and without cross polarisers are also shown in Fig. 7(b,c). The surface to surface separation between the two microspheres is almost equal to the length of the nano-rods as the induced defects of the nano-rods are engulfed. Similar way, we prepared linear chains of alternating micro-rods and nano-rods (Fig. 7(d–f)) and micro-rods, nano-rods followed by microspheres (Fig. 7(g–i)). The binding energy for pair interaction of nano and micro-rods is approximately 3000 kBT. We also prepared a linear chain of quadrupolar microspheres and nano-rods. In this case, the chain is orientated perpendicular to the director. The binding energy for pair interaction is approximately 1500 kBT and comparatively weaker than the previous two cases. These structures are akin to linear copolymer chains. For example, the structure shown in Fig. 7(a,d) can be considered as a linear copolymer of (-A-B-)n type. The structure shown in Fig. 7(g) is akin to a copolymer of (-A-B-C-B-)n type. The linear chain shown in Fig. 5(a) is analogous to a homopolymer of (-A-A-)n type. The polymeric structures are highly stable and reconfigurable by the optical tweezers.
The robustness of the colloidal polymers is tested by applying electric field. Figure 8 shows the effect of ac field perpendicular the chain and the director. With increasing electric field, the chain reorients toward the field direction beyond the Freedericksz’s threshold field since the dielectric anisotropy of 5CB is positive. The reorientation is reversible without creating any deformation in the structure (see SI).

As a next step, the colloidal copolymer chains are assembled by using the laser tweezers for making two dimensional binary crystal. Figure 9 shows a two-dimensional binary colloidal crystal prepared by assembling (-A-B-)n type copolymer chains of nano-rods and microspheres in a planar cell. As a result of long-range elastic interaction a stable 2D oblique lattices are assembled. The diameter of the microspheres and the length of the nano-rods are same i.e., 3 μm. Two colloidal copolymer chains oriented in an antiparallel way and assembled with the help of the optical tweezers. There are 60 dipolar microspheres and 50 nano-rods in the structure shown in Fig. 9(b). The lattice unit is generally a parallelogram with average lattice parameters \( a = 7.2 \mu m \), \( b = 3.9 \mu m \) and angle \( \gamma \approx 48^\circ \). It appears that some microspheres are brighter than others. This means all the colloids are not in one plane. However, the structure is highly stable. More complex colloidal structures can be prepared by designing appropriate polymer as base unit and could be useful for photonic applications.

**Conclusion**

The nano-rods orient very differently than the micro-rods in nematic liquid crystals. The nano-rods exhibit only two specific orientations, namely the parallel or perpendicular, with respect to the nematic director. Majority of them are oriented perpendicular to the nematic director. The induced defects are virtual and hence unresolvable under microscope. On the other hand, micro-rods show all possible orientations unevenly with 50% of them oriented parallel to the director. They are either elastic dipolar or quadrupolar micro-rods. Nano-rods oriented perpendicular to the director experience out-of-plane isotropic attractive quadrupolar interaction in contrast to the...
in-plane anisotropic interaction of the nano-rods oriented parallel to the director. Smaller spherical quadrupolar colloids are unstable and transformed into a dipolar type in the presence of nano-rods. Colloidal chains akin to linear copolymers such as (-A-B-)ₙ, (-A-B-C-B-)ₙ, homopolymer (-A-A-)ₙ, horizontal and vertical ribbons, 2D binary crystals are designed by choosing variety of colloids and directing their assembly by laser tweezers. Polymeric structures are robust as they can be oriented along the applied electric field reversibly without any permanent deformation. Orthogonal orientation of the nano-rods with respect to the nematic director is potential for making hybrid molecular-colloidal liquid crystal system in which the direction of colloidal ordering is

**Figure 7.** POM images of linear chains of colloidal co-assembly of microspheres, micro-rods and nano-rods. Images are taken with (a,d,g,i) crossed polarisers, (b,e,h,k) an additional λ-plate, and (c,f,j,l) without cross polarisers. The diameter of the microsphere is 5.2 μm.
orthogonal to the nematic director. The spontaneous vertical assembly of the nano-rods could provide a unique and versatile route toward building blocks for hierarchical materials assembly.

Materials and Methods
The silica rods were synthesised by a wet chemical method and prepared following the procedure of Kujik et al.\textsuperscript{33}. First, 3 g of PVP (Polyvinylpyrrolidone) was dissolved in 30 ml of 1-pentanol. After complete dissolution of PVP, 3 ml of ethanol (100%, Interchema), 0.84 ml Milli Q water and 0.2 ml aqueous sodium citrate dyhydrate (0.17 M, 99% Sigma-Aldrich) were added. The mixture was shaken thoroughly and made bubble free. Finally, 0.3 ml of Tetraethyl orthosilicate (TEOS, 98% Sigma-Aldrich) was added to the reaction mixture, shaken gently and the reaction was left to continue for 24 h. The mixture was then centrifuged and fractionated to obtain colloids with desired aspect ratio. The average length ($l$) and diameter ($d$) of the silica rods are; $l = 3 \mu m$ and $d = 200 nm$ respectively (designated as nano-rods). We also prepared longer and thicker silica rods of length and diameter; $l = 6.5 \mu m$ and $d = 0.75 \mu m$ respectively (designated as micro-rods). Silica microspheres used in the experiment were obtained from Bangs Chemicals (USA). The scanning electron microscope (SEM) image of the synthesised silica nano-rods is shown in Fig. 1(a). One end of the nano-rods is flat and the other end is hemispherical. They were coated with DMOAP (Octadecyldimethyl-3-trimethoxysilyl propyl-ammonium chloride) that gives homeotropic anchoring of the nematic director and dispersed in 5CB (4-n-pentyl-4-cyanobiphenyl) liquid crystal. The colloidal mixture was introduced in planar cells coated with polyimide AL-1254. A dynamic laser tweezer was built around an inverted optical polarising microscope (Nikon Eclipse Ti-U) using a cw solid-state laser operating at 1064 nm\textsuperscript{32,34–39}. An acousto-optic deflector (Aresis, Tweez 250Si) interfaced with a computer was used for trap movement. The position and orientation of the nano and micro-rods were tracked by using appropriate software with a resolution of $\pm 10 nm$.

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Author Contributions
Surajit Dhara conceived the idea and supervised the work. Muhammed Rasi M performed the experiments. Colloids were synthesised by Ravi Kumar Pujala (Present address: Indian Institute of Science Education and Research, Tirupati). Results were discussed by all and the manuscript was prepared by Muhammed Rasi M and Surajit Dhara.

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