Supplementary Information

A. Experimental

Silica particles were used as model spheres while the rodlike particles were dye-doped sepiolite clay rods with indigo (hereafter referred to as blue rods) or acridine orange (fluorescent rods). The zeolitic channels and indigo dye loading of the sepiolite rods, and the preparation of suspensions of these blue rods were as described in a previous study of dichroism in dye-doped colloidal liquid crystals.¹ Both blue rods and spheres were sterically stabilised in toluene using polymeric stabilisers. The blue rods were treated with SAP-230TP (Infineum), a commercial poly(isobutylene)-based stabiliser² whereas the silica spheres were treated with Hypermer B246 (Uniqema), a commercial *A-B-A* block copolymer with the hydrophobic *A* chains consisting of polyhydroxystearic acid and the *B* hydrophilic part being polyethylene glycol.^{3,4}

Preparation of suspensions of silica spheres. To prepare a suspension of silica spheres, 5 g of silica particles (99.9% 0.5 μ m-diameter silica, Alfa Aesar) were initially dispersed in 100 mL of toluene to give a slurry. This was homogenised for 1 minute with a high-shear mixer (T18 basic Ultra-Turrax, IKA) to break up aggregates and was then ultrasonicated for at least 2 minutes (Ultrawave U500D, Ultrawave). Five grams of Hypermer B246 (hereafter Hypermer), a honey-coloured gel, was added into 200 mL of toluene, which had been previously heated to about 60°C, and stirred in order to dissolve the Hypermer. The silica slurry was then added to the Hypermer solution at room temperature under stirring. This polymer-silica mixture was left stirring overnight and then centrifuged at 5,000 rpm (~4000×g) for 30 minutes. The light yellow supernatant containing free Hypermer was removed and

the sediment redispersed in fresh toluene using a vortex mixer (VX-100, Labnet). The centrifugation procedure was repeated once for the redispersed sediment in order to remove excess Hypermer. The supernatant was replaced by fresh toluene and the sediment of treated particles redispersed using the vortex mixer to yield a Hypermer-treated silica suspension. The final concentration of the suspension was determined by drying known amounts of the suspension. Samples of the blue rods and spheres from stock suspensions were mixed to yield three series of rod-sphere mixtures with blue rod concentrations 3 wt %, 6 wt %, and 9 wt %, each of which with the silica sphere concentration ranging from 1 wt % to 8 wt %. For a comparison, samples of pure rods and spheres were also prepared, at the same concentrations. The vials filled with the mixtures were subsequently placed on a rotating mixer (Rotamix RKVSD, Appropriate Technical Resources), where they were slowly rotated overnight.

Sample concentrations. Experimentally, sample concentrations were determined as mass fractions c_s and c_r (expressed in %) of stabiliser coated particles in solvent, with the subscripts *s* and *r* representing sphere and rod properties respectively throughout this paper. In order to compare with theory and other experimental studies it is useful to evaluate particle volume fractions ϕ . In doing so the thickness δ of the stabilising layer needs to be taken into account, however. The following procedure was therefore employed. The mass fraction 1-*f* of stabiliser in the coated particles was determined by elemental analysis and is reported in Table 1. It is assumed that the stabilising layer on the particles has a mass density $\rho_0 = 0.87$ g cm⁻³ equal to that of the solvent, whereas the density of the core particles (mineral without stabiliser) was measured. For a sample containing both spheres and rods the core particle volume fractions then follow as:

$$\phi_i^{core} = \frac{(f_i c_i / \rho_i)}{(f_s c_s / \rho_s) + (f_r c_r / \rho_r) + (100 - f_s c_s - f_r c_r) / \rho_0}, \text{ where } i = s, r. \text{ (SI-1)}$$

The stabilising layer thickness of the spheres is estimated to be $\delta_s \approx 5 \text{ nm}$ – its effect on the effective volume fraction is small since in any case the stabilising layer in this case is small compared to the particle diameter d_{core} . The effective volume fraction of the spheres then follows as:

$$\phi_s = \phi_s^{core} \left(1 + \frac{2\delta_s}{d_{core}} \right)^3.$$
(SI-2)

Combining Eqs. (SI-1) and (SI-2) and using the characterisation data in Table 1, for a sample containing a low concentration of spheres and no rods, $\phi_s \approx 0.0042c_s$.

For rods the steric layer thickness $\delta_r \approx 4 \text{ nm.}^{5, 6, 7}$ The sepiolite rods were previously found to have a square cross section⁸ so their volume can be written as $V_r^{core} = (D_{core})^2 L_{core}$. In order to compare with theoretical work however it is convenient to model these particles as hard spherocylinders of length *L* and diameter *D*. For the core particles the diameter is chosen to have the same cross section:

$$D_{HSC} = \frac{2}{\sqrt{\pi}} D_{core} , \qquad (SI-3)$$

and the length is chosen to keep the particle volume the same:

$$L_{HSC} = L_{core} - \frac{4}{3\sqrt{\pi}} D_{core}.$$
 (SI-4)

Finally the effective dimensions D and L are obtained by adding $2\delta_{\rm f}$ to these hard spherocylinder dimensions. The effective diameter D, and hence the aspect ratio L/D, are very sensitive to the value of D_{core} as $2\delta_{\rm f}$ is of similar magnitude. From TEM micrographs D_{core} was obtained directly, however in order to allow determining the rod length the image scale was such that 1 pixel corresponded to 1.6 nm – so the value of D_{core} is somewhat inaccurate. In the further analysis of the results therefore D_{core} has been taken as an adjustable parameter. The effective volume fraction of rods is estimated as

$$\phi_r = \phi_r^{core} \left(1 + \frac{2\delta_r}{D_{HSC}} \right)^2.$$
(SI-5)

Assuming $D_{core} = 14$ nm from TEM, for a dilute rod suspension Eqs. (SI-1) and (SI-5) yield $\phi_r \approx 0.0079c_r$.

Preparation of acridine orange-doped sepiolite rods. Acridine orange was used in the preparation of fluorescent dye-doped sepiolite. The molecular width is 4 $Å^9$ slightly smaller than that of an indigo molecule¹⁰ (see Figure SI-1), and the planar molecule can hence enter the zeolitic channels of sepiolite, with cross-sectional dimensions 3.6×10.6 Å².¹¹ The excitation wavelength of acridine orange (~490 nm) is convenient for imaging using a fluorescence confocal microscope with a laser wavelength of 488 nm. Ten grams of sepiolite clay powder (Pangel S9, purified grade supplied by Tolsa, Spain) was added to 350 mL of deionised water under stirring. The mixture was ultrasonicated for 1 minute (Ultrawave U500D, Ultrawave) and homogenised for 1 minute using a high-shear mixer (T18 basic Ultra-Turrax, IKA) to yield a slurry. Then 5 g of acridine orange (hereafter referred to as AO, from Acros Organics) were dissolved in 200 mL of deionised water. The AO solution was added to the sepiolite slurry and the mixture was left stirring slowly at room temperature overnight. The mixture was transferred into glass petri dishes and left in air until dry. Afterwards the mixture was heat-treated in vacuum at 200°C overnight, allowing zeolitic water in sepiolite channels to be replaced by acridine orange. Finally the dved sepiolite was ground with a pestle and mortar.



Figure SI-1. Structures and dimensions of (a) acridine orange and (b) indigo.

Removal of acridine orange from outer rod surfaces. In order to ensure an effective steric stabilization, excess dye was removed from the rod surfaces using Soxhlet extraction with hot methanol for 72 hours.^{1, 12} Once more the dye-doped clay was left in air until dry and ground with a mortar and pestle. The dye content was determined using elemental analysis. Sterically stabilised suspensions of these particles in toluene were obtained using the same procedure employed previously for the blue rods.¹

B. Characterisation

Elemental analysis. The carbon content in both untreated and sterically stabilised particles was analysed using a Carlo Erba elemental analyser (model EA1108) with an estimated accuracy of $\pm 0.3\%$ of the sample mass per measurement. At least three measurements were made for each sample to obtain an acceptable precision.

Surface area measurement. Nitrogen gas adsorption experiments were carried out at 77 K using a Quantachrome Autosorb-1 instrument on silica and sepiolite. The measurement was made for several different pressures and the BET isotherm was employed to describe the adsorption.

Electron microscopy. Transmission electron microscopy (TEM) of the particles was carried out using a JEOL JEM 1200-EX instrument operating at a 120 kV accelerating voltage. The particle size distribution was determined from the micrographs where at least 150 particles were counted. Additionally, the surfaces of the untreated and treated silica spheres were imaged with scanning electron microscopy using a JEOL 6330F field emission instrument operating at a 20 kV accelerating voltage.

Light scattering. Static and dynamic light scattering (SLS and DLS) of the colloidal rods and spheres were carried out to determine the particle sizes. The light scattering measurements were made using a Malvern 4800 Autosizer (Malvern Instruments) equipped with an avalanche photodiode detector and a 532 nm laser source and a stepper motor control of scattering angle. Cylindrical quartz cuvettes (540.110-QS, Hellma) filled with dilute suspensions were thermostatted at 25°C before starting the measurements. Toluene used as a solvent was filtered through a Whatman PTFE syringe filter with a pore size of 0.2 μ m to remove dust. In the SLS experiment, the time-averaged scattered intensity was measured for scattering angles θ ranging from $30^{\circ} - 120^{\circ}$. The scattered intensities were plotted as a function of the wave vector Q,

defined by: $Q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right)$, where *n* and λ are the refractive index of the solvent,

and the laser wavelength in vacuum, respectively. The SLS result for dilute silica spheres was compared to the theoretical form factor calculated from Mie theory using the programme *MIESCAT3*.¹³ The scattering of the blue rods was compared to the theoretical form factor for rods calculated using the programme *LineFit*.¹⁴ In the DLS experiment on a dilute (~0.001 wt %) suspension of Hypermer-treated silica spheres, the diffusion coefficients were determined by analysing the intensity autocorrelation functions at various scattering angles ($30^{\circ} - 120^{\circ}$) with the method of cumulants.^{15, 16} Following the Stokes-Einstein relation, the sphere diameters were subsequently calculated.

Sedimentation and phase behaviour observations. The blue rod-sphere mixtures were filled into rectangular cells with internal dimensions 1 mm × 10 mm × 45 mm (1/G/1, Starna). The cells were left standing in order to observe the sedimentation behaviour. The distance between the meniscus and the supernatant-sediment interface was recorded as a function of time. In addition, the mixtures were observed between crossed polarisers to check for birefringence. Microscopic observations were carried out using either polarising microscopy or differential interference contrast (DIC) microscopy. Polarising microscopy was carried out using an Optiphot-2 polarising microscope (Nikon) equipped with polarising filters, and digital video camera (JVC). DIC microscopy is useful in observing birefringent phases such as a nematic phase; however, DIC microscopy is more suitable for observing the particle assemblies in mixtures whose birefringence is so low that polarising microscopy

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cannot provide a sufficient contrast. Confocal images of samples including fluorescent rods were taken within about 1 hour after preparation using a Zeiss LSM Pascal confocal microscope equipped with a 200 mW/488 nm argon ion laser. Microscopic observations were made in sample cells assembled by glueing a microscope slide with a 1-cm diameter hole at its center onto another slide without a hole. The sample was filled into the hole and covered with a coverslip. Except for the confocal microscopy, the edges of the coverslip were sealed with epoxy glue to prevent the solvent from evaporating.

UV/Visible spectroscopy. Using UV/visible (UV/Vis) spectroscopy, the concentrations of the two species in the mixtures could be determined. To fulfill this analytical approach, it is necessary that absorbances measured at arbitrary wavelength λ from the dilute blue rod-sphere mixtures follow the relation:

$$A_{mix}(\lambda) = \mathcal{E}_r(\lambda)c_r + \mathcal{E}_s(\lambda)c_s, \qquad (SI-6)$$

where $A_{mix}(\lambda)$ is the absorbance of the mixture (equivalent to the overall absorbance). $\varepsilon_r(\lambda)$ and $\varepsilon_s(\lambda)$ are the rod and sphere absorptivities, respectively.

It was previously established that the absorbance of blue rod suspensions (with concentrations up to ~0.2 wt %, in a wavelength range 500 - 800 nm) followed the Beer-Lambert law,¹ and the absorptivity of blue rods had been already determined. Hence in the present study, UV/vis spectra of the dilute Hypermer-treated silica suspensions (with concentrations lower than 0.2 wt %) were measured in a 1 cm path length quartz cuvette (21/Q/10, Starna), from 500-750 nm using a UV/Visible Spectrometer (Hewlett-Packard Agilent 8453E, Agilent Technologies). A toluene background was subtracted. Initially, the Beer-Lambert law for dilute suspensions of the pure Hypermer-treated silica spheres at a given wavelength was verified. The variation in the absorptivity value with the wavelength was then determined.

Afterwards, in order to verify Eq. (SI-6), absorbances measured from the test blue rod-sphere mixtures of known compositions were compared to those calculated following Eq. (SI-6) (see Figure SI-2). Thus least-square fitting allowed determining both c_r and c_s .¹⁷



Figure SI-2. Absorption spectrum of a rod-sphere mixture (solid line) consisting of 0.1 wt % blue rods and 0.16 wt % spheres, compared with the spectrum calculated using the Beer-Lambert law (dashed line). The spectral contributions of the blue rods (dashed-dotted line) and the spheres (dotted line) to the overall spectrum are shown.

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