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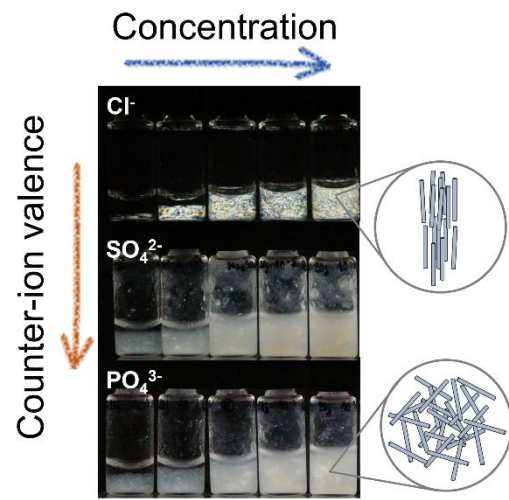
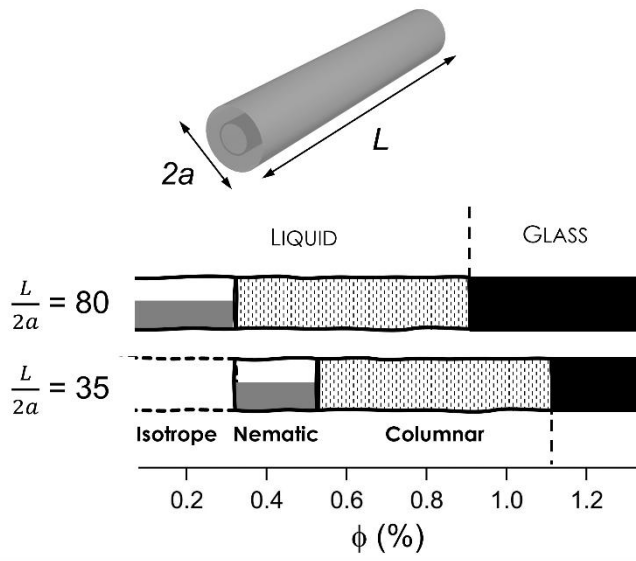
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1 **Graphical abstract:**

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6 **Colloidal phase behavior of high aspect ratio clay nanotubes in symmetric and**
7 **asymmetric electrolytes**

8
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21

22 **Abstract**

23 *Hypothesis:* Imogolite nanotubes (INTs) are unique anisometric particles with monodisperse
24 nanometric diameters. Aluminogermanate double-walled INTs (Ge-DWINTs) are obtained with
25 variable aspect ratios by controlling the synthesis conditions. It thus appears as an interesting
26 model system to investigate how aspect ratio and ionic valence influence the colloidal behavior
27 of highly anisometric rods.

28 *Experiments:* The nanotubes were synthesized by hydrothermal treatment for 5 or 20 days to
29 modify the aspect ratio while the electrostatic interactions were investigated by comparing the
30 colloidal stability in symmetric and asymmetric electrolytes. The phase behavior and their related
31 microstructure were determined by optical observations and small-angle X-ray scattering
32 measurements, coupled with interparticle distance modelling.

33 *Findings:* We revealed that colloidal suspensions of Ge-DWINTs prepared in NaCl are guided by
34 repulsive double layer forces, undergoing different liquid crystal phase transitions before stiffen
35 into a glass-like state. We found that the microstructure can be rationalized by taking into account
36 the anisometric nature of the particles. By contrast, dispersions prepared with asymmetric
37 electrolytes are governed by strong attractive forces and thus form space-filling gels containing
38 large nanotubes aggregates.

39 **Keywords:** imogolite, self-organization, SAXS, columnar phase, glass, gel, phase diagram

40

41 **1. Introduction**

42 Inorganic nanoparticles, whether natural or synthesized, present a wide variety of forms (rods,
43 cylinders, disks, polyhedrons...), making them appealing for applications [1,2]. Most of the
44 shapes are intrinsically anisometric as the aspect ratio between the lengths of the major axis and
45 the minor axis is always larger than 1. The aspect ratio is a fundamental parameter governing the
46 self-organization of anisometric nanoparticles dispersed in a solvent. According to statistical
47 mechanics theories and computer simulations [3–5], anisometric nanoparticles may undergo
48 entropy-driven phase transitions due to excluded-volume interactions. The excluded volume is
49 the effective volume occupied by the particle under the effect of Brownian motion. In the dilute
50 regime, when the nanoparticles are not interacting with each other, it corresponds to a sphere
51 whose diameter is defined by the largest dimension of the objects. In this case, the nanoparticles
52 explore all orientational configurations and the phase is described as isotropic. When the
53 concentration of nanoparticles increases, a competition between orientational entropy (favoring
54 the isotropic phase) and packing entropy (favoring long-range ordered phases) occurs. Another
55 important effect is the presence of surface charges on the nanoparticles that impact their colloidal
56 stability due to a subtle balance of electrostatic interactions. The balance is dependent of the
57 nature (symmetric or asymmetric salts, ion valence) and concentration of the electrolytes, also
58 referred as the ionic strength (I). One way of studying these systems is to explore their phase
59 diagrams as a function of the nanoparticle aspect ratio and volume fraction.

60 A wide variety of anisometric charged nanoparticles display spontaneous phase transitions from a
61 disordered (isotropic) to long-range ordered states (nematic, smectic, lamellar, columnar...) as
62 well as microstructures with arrested dynamics such as gels and glasses with increasing particle
63 concentration [6–11]. A typical example is the colloidal behavior of swelling clay minerals that

64 has been thoroughly explored for almost 100 years due to their large aspect ratio. Observations of
65 lyotropic liquid-crystalline phases have remained elusive until recently with the occurrence of an
66 isotropic-to-nematic phase transition in aqueous dispersions of swelling clay nanosheets
67 (nontronite [12,13], beidellite [14] or fluorohectorite [15,16]). The aspect ratio of 2D clay objects
68 has been proven to influence the resulting colloidal behavior by modifying the position of both
69 the isotropic-to-nematic transition and the sol/glass transition [17,18]. By contrast, the fate of
70 self-organization with one-dimensional (1D) clay nanoparticles such as halloysite or sepiolite
71 received less attention, probably because most of these nanoparticles do not spontaneously
72 present ordered phases unless stabilized by functionalization [19,20]. Beyond 1D clay
73 nanoparticles, phase stabilization is a recurring phenomenon when studying the colloidal stability
74 of objects such as nanotubes. For example, different methods have been explored for dispersing
75 carbon and boron nitride nanotubes [21–26], including covalent functionalization, stabilization
76 with DNA or surface protonation, allowing favorable conditions for the occurrence of nematic
77 liquid crystals. Furthermore, carbon nanotubes present polydisperse diameters and lengths after
78 synthesis, requiring size-sorting procedure. Their aspect ratio has been proved to play a
79 significant role on the electrical, mechanical or thermal properties of carbon nanotubes-based
80 composites [27–29], but not specifically on their colloidal behavior.

81 In this context, imogolite clay nanotubes $(\text{OH})_3\text{Al}_2\text{O}_3(\text{Si,Ge})(\text{OH})$ appear as a perfect model
82 system due to their monodisperse nanometric diameters and the possibility to form stable
83 dispersions in water without functionalization or the use of strong acid [30]. These nanotubes
84 display spontaneously nematic [31–33] and/or hexagonal columnar phases [34,35] when the
85 concentration in particles is increased. The colloidal stability of imogolite nanotubes (INTs) is
86 related to their surface charge, which is mainly due to the protonation of external aluminol groups
87 ($\equiv\text{Al}_2\text{OH}$ and $\equiv\text{Al-OH}$) [36–38]. Typically, the electrophoretic mobility of imogolite nanotubes

88 is always positive (> 40 mV at pH = 7) with a point of zero charge beyond pH = 10 [34,38]. The
89 self-organization of imogolite nanotubes can be controlled by adjusting the range of double layer
90 electrostatic repulsions through the ionic strength (e.g. $I < 10^{-2}$ mol.L⁻¹ for symmetric monovalent
91 salt) [30,39]. An advantage of imogolite nanotubes is the ability to modify their structure by
92 changing either the nature (chloride, perchlorate, nitrate, alkoxide...) or the ratio of the
93 precursors during their hydrothermal synthesis. A slight variation of these parameters can induce
94 structural vacancies in the nanotube walls or modify the morphology, thus dramatically affecting
95 the self-organization behavior [40,41].

96 Studies investigating the specific ion effects (apart from NaCl) on the colloidal stability of 1D
97 objects are limited, to the best of our knowledge, to cellulose nanorods, showing the influence of
98 the nature of the salts on the aggregation kinetics [42] or the modulation of the chiral nematic
99 structure [43]. There is still a gap to be filled to determine how ion specificity effects can
100 modulate the colloidal behavior of stiff nanotubes. Understanding the specific effects of
101 electrolytes is currently of significant interest for bottom-up assembly of anisometric nanotubes
102 into functional metamaterials such as fibers or films [24,26,44]. Most studies on INTs colloidal
103 stability use monovalent salts, generally NaCl. Kobayashi *et al.* recently investigated the
104 influence of ionic valence z and ion specificity (degree of hydration, ligand exchange capacity...) on
105 the stabilization and aggregation of allophane [45–47], a hollow spherical clay nanoparticle
106 with a structural formula close to imogolite. They demonstrated the validity of Derjaguin-Landau
107 and Verwey-Overbeek (DLVO) theory for the accurate prediction of the colloidal stability of
108 these natural spherical nanoparticles with multivalent counter-anions. For asymmetric salts, the
109 magnitude of ion adsorption increases with the ionic valence if the counter-ions are oppositely
110 charged to the particle [48]. Nevertheless, these nanostructures show no liquid crystal phase
111 transitions unlike INTs.

112 Drawing on these previous studies, we investigate how the phase diagram of anisometric
113 imogolite nanotubes is affected by asymmetric salts with respect to symmetric electrolytes while
114 varying the aspect ratio (length/diameter) of the nanotubes. We synthesized aluminogermanate
115 double-walled imogolite analogues (Ge-DWINTs) by adjusting the hydrothermal aging time (5 or
116 20 days) [49]. Series of dispersions with controlled ionic strength (10^{-3} mol.L⁻¹) were prepared
117 with NaCl, Na₂SO₄ or Na₃PO₄ electrolytes. The value of the imposed strength was chosen based
118 on previous studies showing that below 10^{-2} mol.L⁻¹, Ge-DWINTs dispersions are colloiddally
119 stable [30,39,41]. All the samples were characterized by coupling optical microscopy and small-
120 angle X-ray scattering experiments. We explained the evolution of the microstructure on the basis
121 of an effective geometrical approach taking into account the anisometric nature of the nanotubes.
122 Finally, a complete phase diagram is established, where the effect of the ionic valence is
123 discussed with respect to the nanotube concentration and aspect ratio.

124 **2. Material and Methods**

125 **2.1. Synthesis of Ge-DWINTs with different aspect ratio**

126 Aluminogermanate double-walled imogolite nanotubes were obtained following the procedure
127 described by Amara *et al.* [50]. An aqueous solution of aluminum perchlorate nonahydrate (C =
128 0.2 mol.L⁻¹, reagent grade, Alfa Aesar), tetraethoxygermane ($\geq 99.95\%$, Sigma-Aldrich) and urea
129 ($\geq 99\%$, Sigma-Aldrich) was prepared under stirring with a molar ratio of [Al]:[Ge]:[urea] equals
130 to 2:1:2. The choice of hydrated perchlorate instead of anhydrous salt has been made to minimize
131 any risk of exothermic reactions when mixing aluminum salt with water. The mixture was then
132 transferred into a PTFE-lined acid digestion vessel (Parr Instrument) for hydrothermal aging
133 during 5 or 20 days, referred to as DW_{5d} and DW_{20d} in the following. After hydrothermal
134 treatment, the resulting suspensions were washed with ultrapure water using semipermeable

135 dialysis membranes (Spectra/Por®, cutoff = 10 kDa). The water bath was renewed at least 10
136 times thus allowing the conductivity to be dropped below 0.5 mS.cm⁻¹ [51]. Transmission
137 electron microscopy (TEM) experiments were performed to determine the length distribution of
138 the nanotubes. For both DW_{5d} and DW_{20d}, a dispersion was prepared at 1 mg.L⁻¹ in ethanol and a
139 drop of it was deposited on a standard carbon-coated copper grid. TEM observations were carried
140 out on a JEOL 1400 microscope operating at 80 kV. Image analysis was realized using Fiji
141 software [52].

142 **2.2. Colloidal dispersions with controlled ionic strength**

143 Concentrated samples were prepared by osmotic stress by maintaining during two weeks
144 semi-permeable membranes filled with DW_{5d} and DW_{20d} stocks in a 2L beaker containing a
145 polyethylene glycol solution (M_w = 20000 g.mol⁻¹, C = 20 g.L⁻¹). An appropriate amount of
146 NaCl, Na₂SO₄ or Na₃PO₄ salts was added to keep a constant ionic strength *I*, fixed at 10⁻³ M,
147 according to:

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \quad (1)$$

148 with *c_i* the molar concentration of ions, *z_i* the charge number of ions and the index *i* runs over
149 all the ions in the solution. After completion of the osmotic stress, the dispersions were recovered
150 and their volume fractions ϕ ($\phi = C/\rho_{INT}$ with *C* the solid concentration of Ge-DWINTs and
151 ρ_{INT} the density of a nanotube taken as 3.6 g.cm⁻³ [44]) were determined by weight loss upon
152 drying during 24h. For each batch, a series of samples has been prepared by dilution with the
153 appropriate salt solution at *I* = 10⁻³ M to obtain dispersions with varying volume fraction ranging
154 from 0.07 to 2%. Macroscopic optical observations were performed using a home-made
155 polarized-light observation setting equipped with a Panasonic DMC-FZ18 digital camera.

156 Polarized optical microscopy (POM) was carried out on a BX51-P (Olympus, Japan) either
157 without or with the use of a retardation filter (l-plate at 530 nm) placed at 45° with respect to the
158 polarizers. Images were acquired with a sCMOS color camera (sCMEX-20, Euromex,
159 Netherlands). Aqueous dispersions were sucked into flat glass capillaries (0.2 x 2 mm, VitroCom,
160 USA), which have been flame-sealed and stored vertically prior to POM observations.

161 **2.3. Small-Angle X-ray scattering (SAXS)**

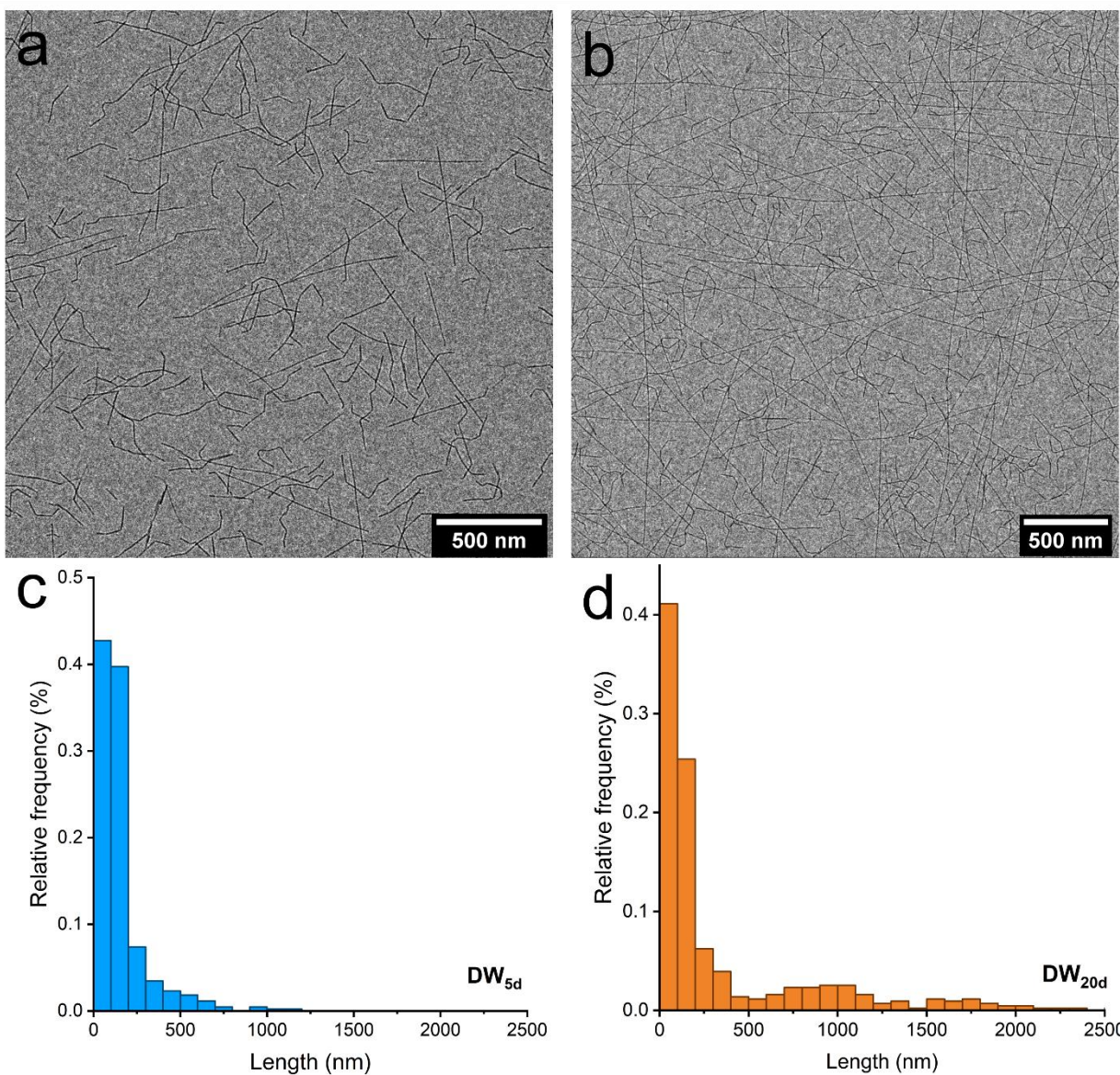
162 Synchrotron-based SAXS experiments were realized at the SWING beamline (SOLEIL
163 synchrotron, Saint-Aubin, France) and a fixed wavelength $\lambda = 1.0332 \text{ \AA}$. The scattering patterns
164 were collected on a two-dimensional detector (Eiger 4M, Dectris Ltd., Switzerland) placed at a
165 distance of 6.2 m of the sample in a vacuum tunnel. Prior to SAXS experiments, aqueous
166 dispersions were transferred in cylindrical borosilicate glass capillaries (WJM Glas/Müller
167 GmbH, DE) that were flame-sealed and stored vertically. Angular integration of the scattering
168 patterns, giving the dependence of the scattered intensity as a function of the scattering vector
169 modulus Q ($Q = 4\pi \sin(\theta) / \lambda$ with 2θ is the scattering angle) was processed by homemade
170 software.

171 **3. Results and discussion**

172 **3.1. Characterization of the nanotubes batches**

173 We have demonstrated recently that long reaction times (> 5 days) further increase the length
174 distribution and thus the aspect ratio [49]. The completion of Ge-DWINTs is attested by infrared
175 spectroscopy and X-ray scattering (Figure S1), showing the classic signatures associated with
176 these nanotubes (see Supporting Information). As shown previously, the synthesis conditions
177 ensure the absence of polydispersity in the number of walls [50] and the outer radius a of double-
178 walled aluminogermanate nanotubes is around 2.2 nm [40]. Transmission electron microscopy

179 observations and the related length distribution (Figure 1) confirm an increase in the proportion
180 of tubes longer than 500 nm for DW_{20d}. In both 5 days and 20 days batches, nanotubes length
181 follows a log-normal distribution with a mean value L around 150 nm for DW_{5d} and 350 nm for
182 DW_{20d}. Moreover, the latter presents a significant proportion of nanotubes with length around
183 900 nm.

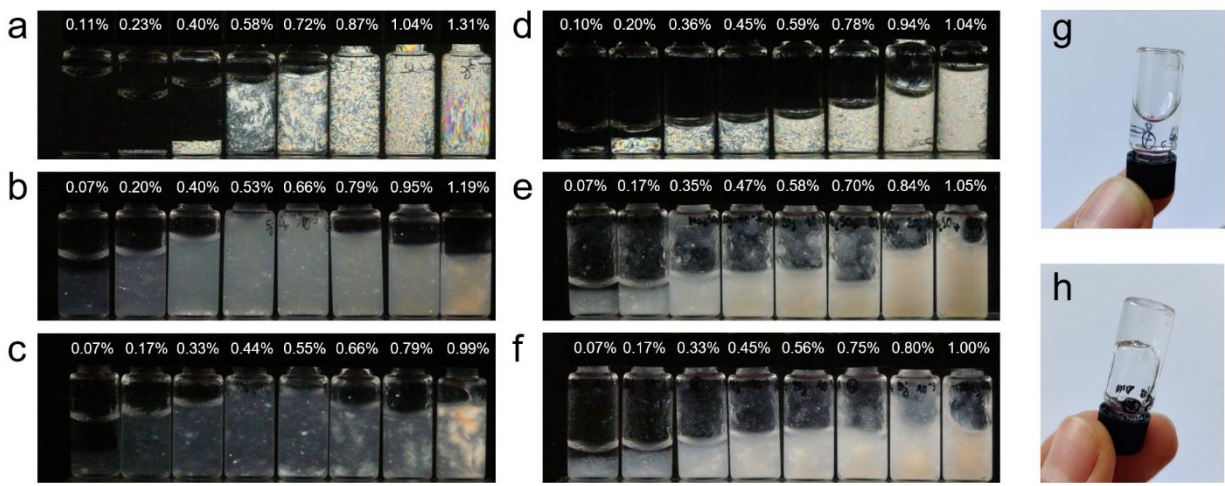


184

185 **Figure 1.** Representative TEM images of Ge-DWINTs batches obtained after (a) 5 days and (b)
186 20 days of hydrothermal reaction. Corresponding histograms of length distribution for (c) DW_{5d}
187 and (d) DW_{20d}.

188 **3.2. Phases transitions vs aggregation**

189 Liquid-crystal (LC) phases can be revealed by studying the optical properties of the dispersions.
190 Using NaCl to control the ionic strength allows the formation of stable Ge-DWINTs suspensions
191 that are optically transparent under visible light [40]. By choosing thoroughly the initial
192 precursors, typically perchlorate anions, these Ge-DWINTs dispersions can exhibit a rich liquid-
193 crystalline phase behavior at low volume fraction (down to 0.2%) [40]. By contrast, dispersions
194 of Ge-DWINTs prepared with Na₂SO₄ or Na₃PO₄ electrolytes are turbid under visible light
195 suggesting the presence of larger structures rather than individual nanotubes. Investigations of the
196 phase behavior of Ge-DWINTs dispersions at a fixed ionic strength ($I = 10^{-3}$ mol.L⁻¹) controlled
197 by these different salts (NaCl, Na₂SO₄ and Na₃PO₄) are conducted as a function of the nanotube
198 volume fraction and for each nanotube aspect ratio. Glass vials filled with these dispersions were
199 left in an upright position during one month to ensure reaching thermodynamic equilibrium.
200 Figure 2 presents the birefringence of Ge-DWINTs dispersions featured by naked-eye
201 observations between crossed-polarizers.



202
 203 **Figure 2.** Macroscopic optical observations between crossed polarizers of (a-c) DW_{5d} and (d-f)
 204 DW_{20d} aqueous dispersions prepared at different volume fractions ϕ and electrolytes ($IS = 10^{-3}$
 205 mol.L^{-1}). (a,d) NaCl; (b,e) Na_2SO_4 ; (c,f) Na_3PO_4 . Photographs of DW_{20d} aqueous dispersions with
 206 NaCl (g) in a liquid state ($\phi = 0.36\%$) and (h) above the glass transition ($\phi = 0.94\%$). The latter
 207 does not flow upon tube reversal.

208 In the case of NaCl electrolyte (Figure 2a,d), suspensions of Ge-DWINTs exhibit an isotropic
 209 phase at low volume fractions (less than 0.10%). A spontaneous phase separation occurs beyond
 210 a certain volume fraction (DW_{5d} : $\phi > 0.2\%$; DW_{20d} : $\phi \sim 0.1\%$) as shown by the coexistence of an
 211 isotropic phase with a denser birefringent LC phase. The isotropic phase at the top of the vial
 212 displays streaming birefringence when the samples are disturbed. This simple visual test tells us
 213 that the isotropic phase contains nanotubes, aligning within the flow upon shearing. The phase
 214 separation results from a thermodynamic equilibrium, the co-existence of the isotropic and LC
 215 phases reflecting a first order transition. The proportion of the birefringent phase raises with
 216 increasing the total volume fraction. By further increasing the volume fraction, liquid dispersions
 217 (Figure 2g) stiffen to form homogenous and transparent arrested phases (Figure 2h). These
 218 arrested phases remain birefringent between crossed polarizers, indicating that the nanotubes

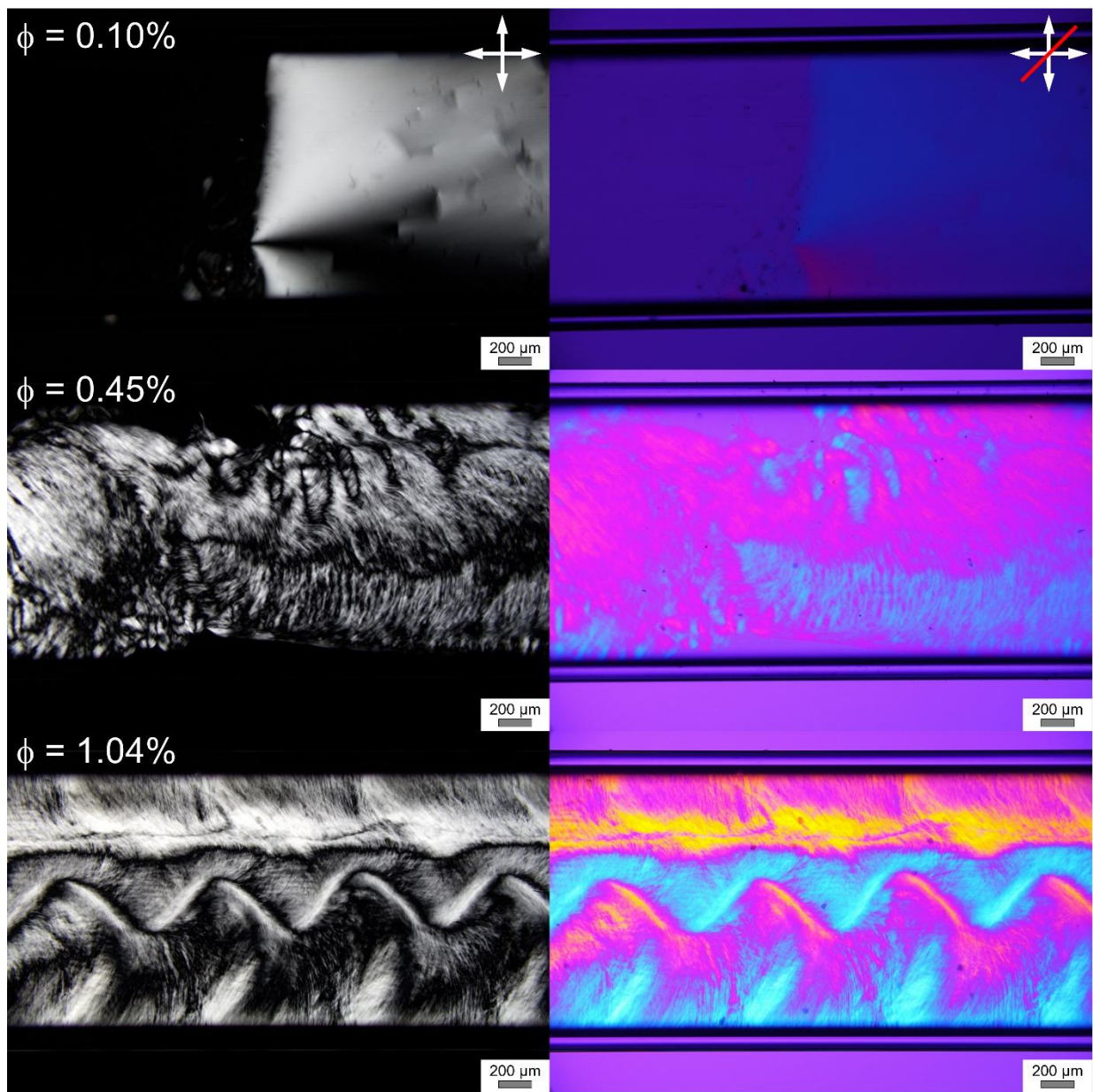
219 have a preferred orientation. They can therefore be considered as a glass-like state, where the
220 slowing of the nanotubes dynamics is due exclusively to excluded volume effects [6].

221 For dispersions prepared with divalent and trivalent salts (Figure 2b-f), the samples remain turbid
222 with in some cases the presence of large and birefringent domains. A phase separation is
223 observed only for the lowest volume fractions but the upper isotropic phase does not show any
224 birefringence under flow. The phase separation is only due to the aggregation of nanotubes,
225 which end up sedimenting in the vials. For $\phi > 0.2\%$, the samples display an arrested behavior,
226 blocking the separation of large nanotubes clusters, independently of the nanotube aspect ratio. In
227 this case, these samples can be considered as gels due to the attractive nature of the interactions.

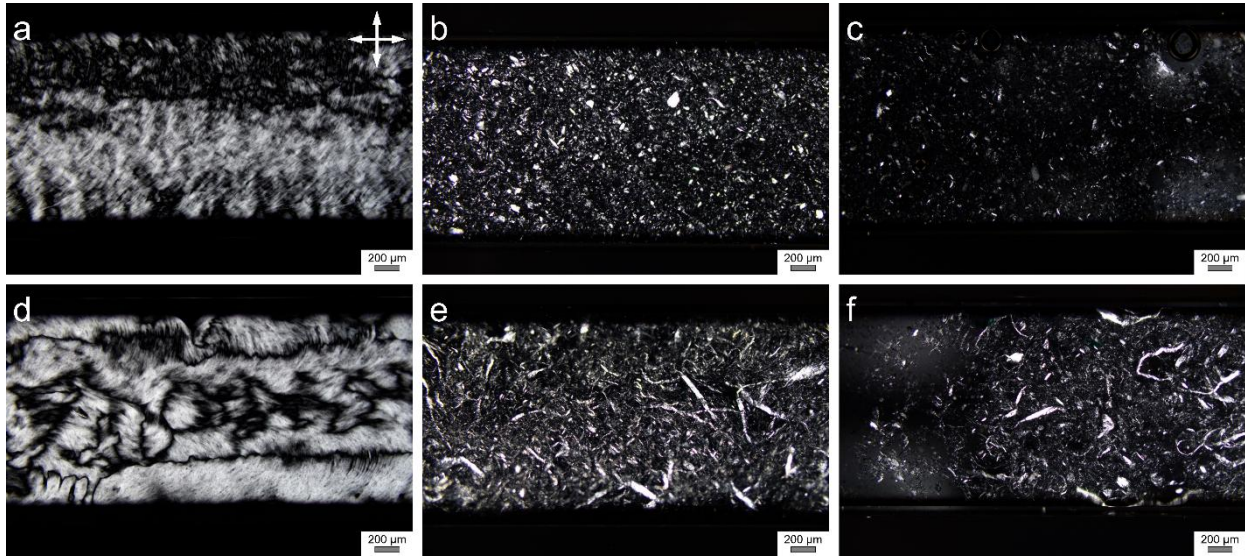
228 **3.3. Optical textures at the microscopic level**

229 The nature of the different phases can be assessed through the study of the optical texture of the
230 dispersions using polarized optical microscopy (POM). Representative POM images of DW_{5d} and
231 DW_{20d} dispersions prepared in NaCl (Figure S2 and Figure 3) present various optical textures
232 related to different LC phases as the volume fraction increases. In the case of DW_{20d} at $\phi =$
233 0.10%, POM image displays a clear separation between an isotropic phase and a birefringent one.
234 The texture is typical of the nematic phase [14,34], with smooth bright and dark regions related to
235 the structural defects (disclinations lines) between the domains oriented in different directions as
236 shown by observing the sample using a retardation filter while tilting the sample by $\pm 45^\circ$
237 clockwise (Figure S3). In these images, blue (pink) regions correspond to an orientation of the
238 nanotube long axis parallel (perpendicular) to the slow axis of the retardation filter. While
239 increasing the concentration up to 0.45%, pleated ribbon like areas of aligned nanotubes are
240 observed, highlighted by the modification of the optical paths when the λ -plate is inserted (Figure
241 3). This texture corresponds to the typical hexagonal columnar phase [40]. At higher

242 concentration ($\phi = 1.04\%$), DW_{20d} dispersions in NaCl form birefringent arrested phases that
243 show flow alignment texture. The evolution of the optical textures for DW_{5d} dispersions in NaCl
244 are similar although the phase transitions do not occur at the same volume fractions (Figure S2).
245 The optical textures for samples with multivalent salts differ significantly since no LC phase can
246 be identified (Figure 4). Ge-DWINTs dispersions prepared in Na_2SO_4 and Na_3PO_4 display almost
247 similar POM images with the presence of birefringent aggregates whatever the concentration.
248 However, the size and shape of the aggregates differ with the aspect ratio of the nanotubes as
249 illustrated from POM images in Figure 4. Rounded aggregates are obtained with DW_{5d} samples
250 as those observed previously for single-walled aluminogermanate nanotubes (aspect ratio around
251 11) [51], while the structures are more elongated for the highest nanotube aspect ratio.



252
 253 **Figure 3.** Polarized optical microscopy observations of DW_{20d} aqueous dispersions prepared at
 254 different volume fractions ϕ with NaCl ($IS = 10^{-3} \text{ mol.L}^{-1}$). The images on the right are taken with
 255 the addition of a retardation filter (λ -plate, 530 nm). The white arrows and the red line indicate
 256 the orientation of the polarizers and the slow axis of the retardation filter, respectively.



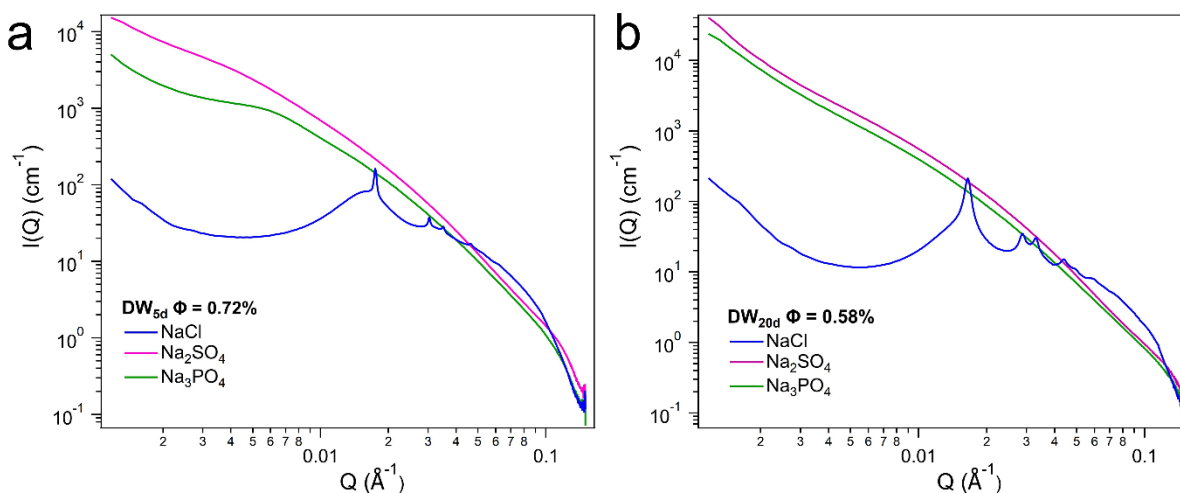
257
 258 **Figure 4.** Effect of the electrolyte type on optical textures of (a-c) DW_{5d} ($\phi \sim 0.4\%$) and (d-f)
 259 DW_{20d} ($\phi \sim 0.35\%$) aqueous dispersions. (a,d) NaCl; (b,e) Na₂SO₄; (c,f) Na₃PO₄.

260 3.4. Structure of dispersions

261 Small angle X-ray scattering (SAXS) experiments were conducted to confirm and assess
 262 unambiguously the structure of the different dispersions. The measurements were performed after
 263 vertical storage of the capillaries for one month to ensure phase separation. When the sample
 264 exhibits an isotropic/birefringent phase separation, the scattering intensity shown in the following
 265 figures is that of the birefringent part. An example of a scanning along the capillary is presented
 266 in Figure S4.

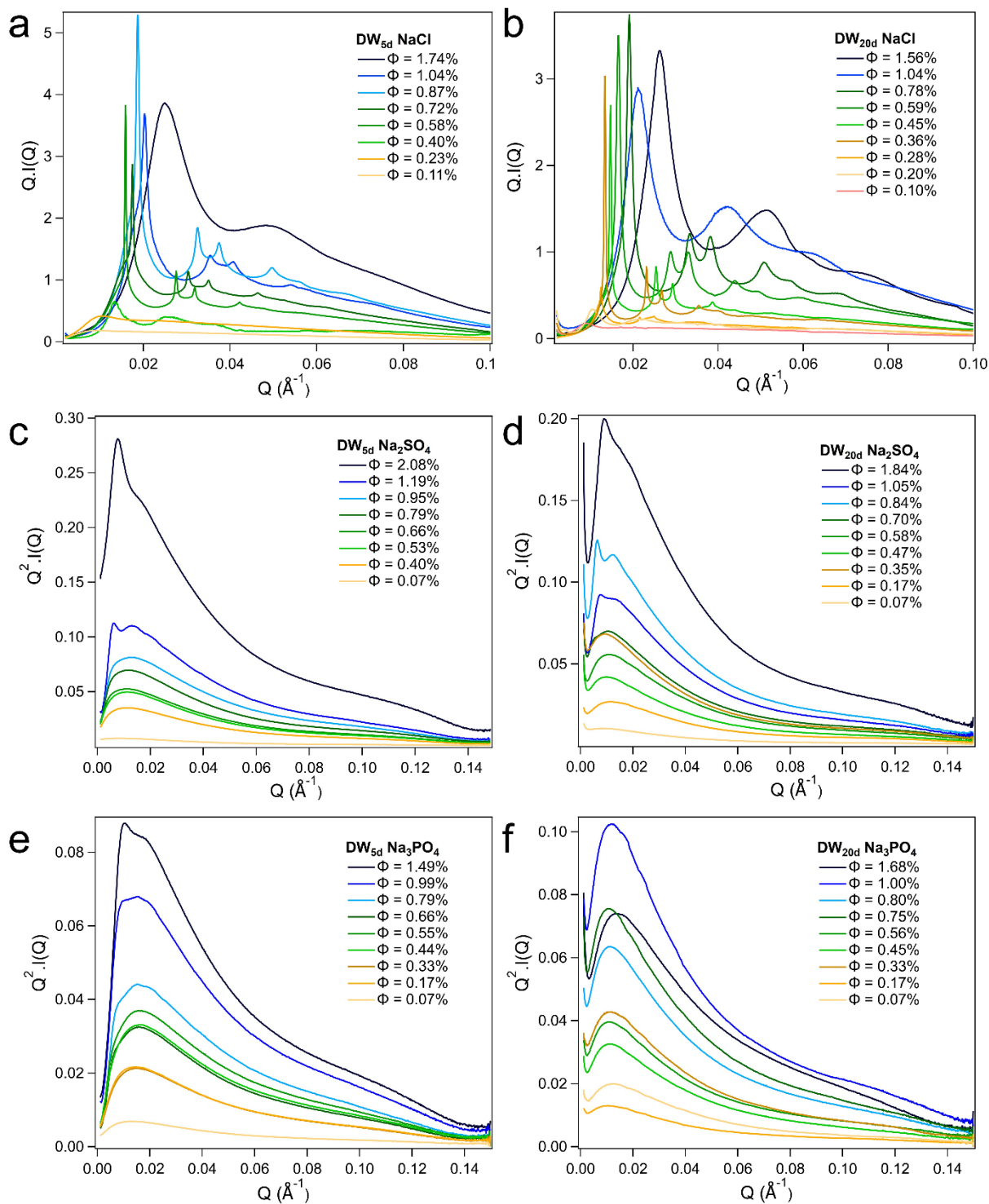
267 Scattering intensities are first analyzed at a fixed volume fraction, chosen to compare dispersions
 268 in multivalent salts with dispersions in NaCl presenting a liquid-crystal organization. As shown
 269 in Figure 5, scattering intensities differ significantly between dispersions with monovalent and
 270 the multivalent salts. DW dispersions in NaCl present at least four sharp peaks with Q-values
 271 following the ratio $1:\sqrt{3}:2:\sqrt{7}$. The ratios between the peak positions correspond to that in a
 272 two-dimensional hexagonal reciprocal lattice in the columnar hexagonal (Col_H) phase [34,40,53].

273 In the middle-Q region [0.01-0.1 \AA^{-1}], the curve is decreasing as $I(Q) \sim Q^{-1}$, which is typical of
 274 one-dimensional objects [54]. By using multivalent salts, the scattering intensity decays as $I(Q) \sim$
 275 Q^{-2} , whatever the nanotube aspect ratio. The exponent value of 2 suggests the formation of bi-
 276 dimensional aggregates in the system. We also notice the presence of a broad modulation around
 277 $Q \sim 6.10^{-3} \text{\AA}^{-1}$, which could be related to a characteristic average distance in the aggregates.



278
 279 **Figure 5.** Evolution of the scattering intensity $I(Q)$ as a function of the scattering vector Q for (a)
 280 DW_{5d} and (b) DW_{20d} dispersions prepared in different salts (NaCl, Na_2SO_4 and Na_3PO_4) at a
 281 fixed volume fraction of $\phi = 0.72\%$ and $\phi = 0.56\%$ respectively.

282 In order to magnify the correlation peaks, we have converted the scattered intensities $I(Q)$ to
 283 obtain the structure factors $Q \cdot I(Q)$ for NaCl and $Q^2 \cdot I(Q)$ (or Kratky plots) for asymmetric
 284 electrolytes (Na_2SO_4 and Na_3PO_4). The resulting curves for the different aspect ratio and volume
 285 fractions are presented in Figure 6.

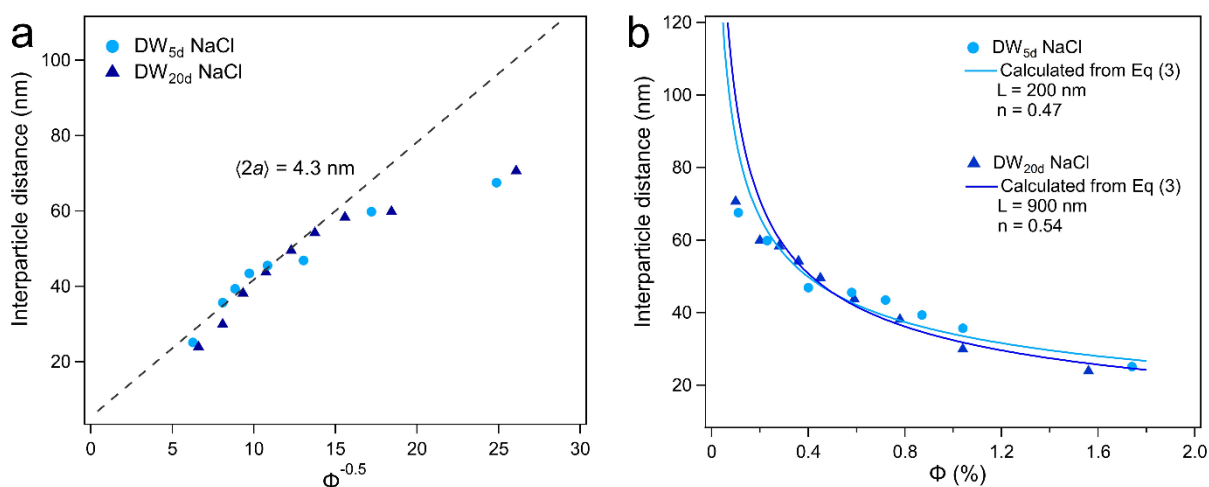


286
 287 **Figure 6.** Evolution of the structure factors as a function of the scattering vector Q for DW_{5d}
 288 (*left*) and DW_{20d} (*right*) dispersions at various volume fractions ϕ with (a,b) NaCl; (c,d) Na_2SO_4
 289 and (e,f) Na_3PO_4 electrolytes.

290
 291 As anticipated, the evolution of the scattering curves as a function of the volume fraction differ if
 292 monovalent anion is used compared to di or trivalent ones, the latter showing only a fairly broad
 293 correlation peak. Therefore, bi-dimensional aggregates are present with multivalent salts
 294 independently of the volume fraction. For dispersions prepared in NaCl, the SAXS patterns
 295 obtained at low volume fractions ($\phi \leq 0.2\%$) present only several broad scattering peaks, arising
 296 from short-range positional order of the nanotubes in a nematic phase [11,34]. For higher volume
 297 fraction, the observed liquid-crystal phase is of the hexagonal columnar (Col_H) type with the
 298 sharp scattering peaks as described above. The positions of these peaks shift towards high Q-
 299 region, which corresponds to a decrease of the distance between nanotubes, while increasing
 300 concentrations. This is a proof that the interactions are dominated by excluded-volume effects in
 301 these dispersions. Finally, once the arrested phase is reached, the scattering curves present only
 302 broad periodic modulations of the scattered intensity as in the nematic phase. In this case, the
 303 short-range positional order is induced by frustrated orientational and translational motion of the
 304 nanotubes in the glass state. Here again, the increase in volume fraction in the arrested phase
 305 induces a decrease of the interparticle distance revealed by the shift of the modulations towards
 306 high Q-region.

307 The average interparticle distance $\langle d \rangle$ either in the nematic phase or the arrested phase is
 308 calculated from the positions of the first peak as $\langle d \rangle = 2\pi/Q_{max}$. For hexagonal columnar phase,
 309 the interparticle distance corresponds to the 2D lattice parameter of the phase $\langle d_{ColH} \rangle$ that can be
 310 retrieved by plotting the Q_{hk} vs $\sqrt{h^2 + k^2 + hk}$, with hk the reflections indexed according to a
 311 2D hexagonal lattice. The lattice parameter then depends on the slope γ of this curve as
 312 $\langle d_{ColH} \rangle = \frac{4\pi}{\sqrt{3}\gamma}$. For charged nanotubes where the packing entropy term prevails over interparticle

313 correlations, a 2D hexagonal configuration of parallel nanotubes is expected [55]. This model
 314 predicts that the average interparticle distance scales as $\phi^{-0.5}$. Figure 7a shows that experimental
 315 interparticle distances obtained at high volume fractions (low $\phi^{-0.5}$ values) display this linear
 316 dependence whatever the nanotube aspect ratio.



317

318 **Figure 7.** (a) Evolution of the interparticle distance deduced from SAXS curves as a function of
 319 $\phi^{-0.5}$. The dotted line corresponds to the model described in Eq. (2). (b) Interparticle distance as a
 320 function of Ge-DWINTs volume fraction ϕ . The lines correspond to the fit calculated from Eq.
 321 (3).

322 The deviation for $\phi^{-0.5} \sim 15$ corresponds to the point at which the hexagonal columnar phase
 323 predominates, according to POM and SAXS results. We would therefore have a three-
 324 dimensional swelling when the nanotubes are in a nematic or isotropic phase. Conversely, the
 325 organization of the nanotubes on 2D hexagonal lattice induces a two-dimensional swelling of
 326 one-dimensional objects in the direction perpendicular to the nanotube axis. When the glass state
 327 is reached, the nanotubes lose degrees of freedom in both rotation and orientation, trapped in a
 328 sort of cage defined by their neighbors. In this configuration, the slope of the curve is directly
 329 related to the average outer nanotube diameter $\langle 2a \rangle$ [55] such as:

330
$$\langle d \rangle = \left(\frac{\pi\sqrt{3}}{8} \right)^{\frac{1}{2}} \langle 2a \rangle \phi^{-0.5} \quad (2)$$

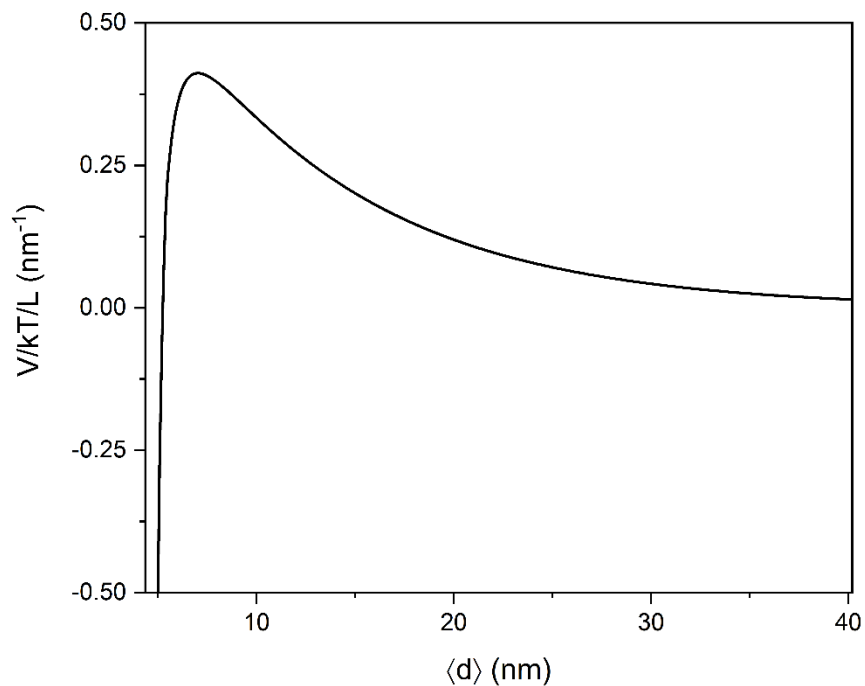
331 By using eq. (2), we find a value of $\langle 2a \rangle \sim 4.3$ nm, which is in good agreement with the outer
 332 diameter of Ge-DWINTs as determined previously [40]. If we perform the same analysis on
 333 dispersions prepared with divalent or trivalent electrolytes, the position of the correlation peaks
 334 derived from SAXS curves vary widely without any relationship to volume fraction and nanotube
 335 aspect ratio (Figure S5). This suggests a heterogeneous aggregation of imogolite nanotubes under
 336 current experimental conditions.

337 A limitation of the model presented in eq. (2) is that it is limited to the high-volume fraction
 338 regime and does not reflect the overall trend of the interparticle distances. Baravian *et al.*
 339 demonstrated that simple geometrical considerations can predict accurately the evolution of the
 340 interparticle distances from the dilute to the concentrated regime [56]. In the case of repulsive 1D
 341 objects, the average interparticle distance writes:

342
$$\langle d \rangle = \frac{L}{\left(\frac{\phi_{eff}}{\phi_{eff}^*} \right)^{1/3} + \left(\frac{\phi_{eff}}{\phi_{eff}^*} \right)^n} \quad (3)$$

343 ϕ_{eff} is the effective volume fraction of a virtual sphere encompassing the particles, which is
 344 equivalent to $\phi \frac{2}{3} \left(\frac{L}{\langle 2a \rangle} \right)^2$ for nanotubes where ϕ_{eff}^* is the critical volume fraction corresponding
 345 to the packing limit. Baravian *et al.* [56] demonstrated that the maximum packing is $\phi_{eff}^* = 1$,
 346 considering that the virtual spheres encompassing the particles are deformed leading to a dense
 347 packing of prolate ellipsoids [56]. By using this model and the nanotube diameter of 4.3 nm
 348 determined previously, the experimental interparticle distances are well reproduced with a value
 349 of $n \sim 0.5$ (i.e. the theoretical value for 1D objects) and an average nanotube length L of 200 and
 350 900 nm for DW_{5d} and DW_{20d}, respectively (Figure 7b). These parameters are similar with the
 351 values obtained from TEM analysis and suggests that the fraction of large particles predominates

352 in the resulting structural organization. Considering the good agreement between experimental
353 and calculated interparticle distances, it is possible to calculate the energy of interactions V
354 between two parallel and charged cylindrical nanoparticles through the DLVO theory [57]. This
355 corresponds to the sum of repulsive electrostatic forces (V_R) due to the diffuse double layer of
356 ions and the van der Waals attractive energy (V_A) that are both dependent of the nanotube length.
357 Details are provided in Supplementary Material. We report in Figure 8 the total energy of
358 interaction per nm (V/L) at $T = 298$ K and for a ionic strength of $I = 10^{-3}$ mol.L $^{-1}$. Large repulsive
359 maximum is found at $\langle d \rangle \sim 7.1$ - 7.2 nm. This calculation confirms that for monovalent electrolyte
360 and low ionic strength, imogolites nanotubes are stabilized by strong Coulombic forces via
361 electrical double-layer interactions.

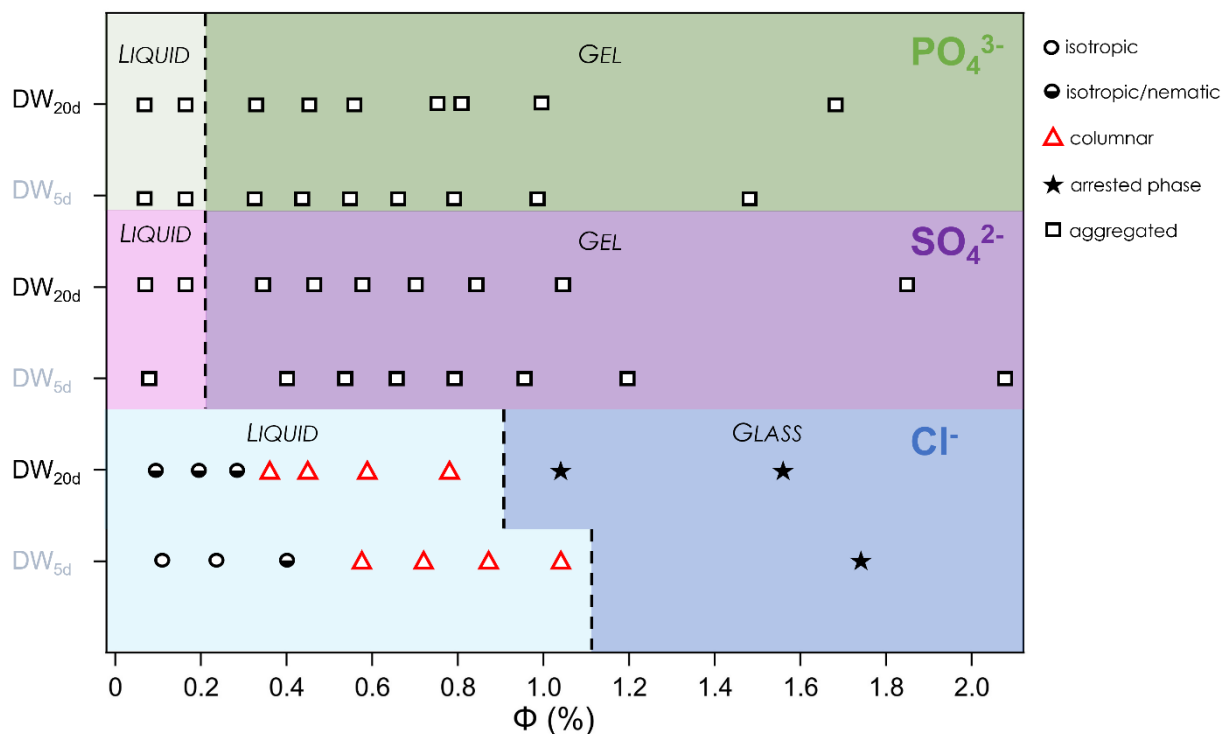


362
363 **Figure 8.** Energy of interaction per nm as a function of the interparticle distance for aqueous
364 dispersions of imogolite nanotubes. Calculations are performed at room temperature for an ionic
365 strength $I = 10^{-3}$ mol.L $^{-1}$, a surface potential $\psi_0 = 50$ mV, a Hamaker constant $A = 6.7 \times 10^{-20}$ J
366 and a nanotube radius $a = 2.2$ nm (see text for details).

367

368 **3.5. Phase diagram**

369 Collectively, these results allow us to build a phase diagram relating the charge valence of salts
370 with respect to the nanotube volume fraction for both aspect ratios (Figure 9). For imogolite
371 nanotubes prepared in asymmetric electrolytes, all our experimental results show a predominance
372 of van der Waals attraction between the nanotubes. Batches with Na_2SO_4 and Na_3PO_4 exhibit
373 similar behavior with the sticking of imogolite nanotubes forming large aggregates that settle
374 down for volume fraction lower than $\phi = 0.2\%$. Beyond, all the samples form stiff gels,
375 independently of the aspect ratio. The formation of larger aggregates at low ionic strength could
376 be due to a bridging effect between the nanotubes through the di/trivalent ions, also known as the
377 “egg-box” effect [58]. Studies at various ionic strength could be used to determine the critical
378 ionic strength leading to the aggregation of the system and the transition from a glass to a gel
379 state for volume fraction higher than $\phi = 0.2\%$.



380
 381 **Figure 9.** Phase diagram as a function of Ge-DWINTs volume fraction ϕ for DW_{5d} and DW_{20d}
 382 with NaCl , Na_2SO_4 and Na_3PO_4 salts. The dotted lines between the different regimes are to guide
 383 the eyes.

384 Imogolite nanotubes dispersed in NaCl present a rich phase diagram with different liquid-
 385 crystalline phases (nematic and hexagonal columnar) as a function of the volume fraction. The
 386 system becomes totally “frozen” beyond a critical volume fraction, close to 1%. The nanotubes
 387 are stiffen into a glass-like state where the tubes are non-aggregated but have limited rotational
 388 and translational motion with a nematic-like ordering.

389 From the phase diagram in Figure 9, we notice that the onsets of the liquid-crystal and sol/glass
 390 transitions are shifted to lower volume fraction as the aspect ratio of the nanotubes increases.
 391 Typically, the glass-like state is observed at $\phi = 0.9\%$ for DW_{20d} and $\phi = 1.1\%$ for DW_{5d} . This is
 392 reminiscent of the theoretical predictions by Vold that the critical volume fraction at which the
 393 arrested phase occurs decreases with increasing the particle aspect ratio [59]. Thus, tuning the

394 nanotube length provides control over the self-organization of imogolite nanotubes and can be
395 used to shift the onset of the arrested phase.

396 **4. Conclusion**

397 We investigated the role of the aspect ratio on the self-organization of anisometric charged
398 nanotubes in presence of symmetric and asymmetric electrolytes at low ionic strength (10^{-3}
399 mol.L⁻¹). We demonstrated that divalent (SO₄²⁻) or trivalent (PO₄³⁻) anions induce aggregation of
400 the nanotubes. The formation of aggregates and their related microstructure does not depend on
401 the nanotube aspect ratio nor the volume fraction. This behavior suggests a heterogeneous
402 aggregation process. By contrast, colloidal dispersions of Ge-DWINTs in NaCl display a rich
403 phase behavior with the occurrence of true liquid-crystal phases (nematic and hexagonal
404 columnar phase) before reaching a glassy-like state. We also found that the microstructure is
405 affected by the anisometric nature of the particles, allowing to describe the colloidal organization
406 from the dilute state to the arrested phase. The predominance of repulsive interactions is
407 confirmed from calculations of the interaction potential. The potential decays with decreasing
408 aspect ratio of the nanotubes, increasing the stability range of the liquid-crystal phases before
409 reaching an arrested state. Compared to previous works on colloidal assembly of 1D objects
410 [19,20,24], we have demonstrated that the onset of phase transitions strongly depends on the
411 nanotube aspect ratio; the higher the ratio, the lower the critical volume fraction. This was made
412 possible by the ability to finely control the aspect ratio of the nanotubes during synthesis. This
413 makes imogolite nanotubes attractive as a model system for further experimental and theoretical
414 experiments concerning the colloidal stability of charged 1D nanoparticles and the relation
415 between structure and viscoelastic properties [60,61]. This study open up prospects for probing
416 interactions with more complex electrolytes such as ionic liquids for application in batteries

417 [62,63]. It also provides new perspectives to develop novel structured materials by triggering the
418 self-organization through external stimuli [64,65].

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- 602

603

604 **Figure captions**

605 **Figure 1.** Representative TEM images of Ge-DWINTs batches obtained after (a) 5 days and (b)
606 20 days of hydrothermal reaction. Corresponding histograms of length distribution for (c) DW_{5d}
607 and (d) DW_{20d} .

608
609 **Figure 2.** Macroscopic optical observations between crossed polarizers of (a-c) DW_{5d} and (d-f)
610 DW_{20d} aqueous dispersions prepared at different volume fractions ϕ and electrolytes ($IS = 10^{-3}$
611 mol.L^{-1}). (a,d) NaCl; (b,e) Na_2SO_4 ; (c,f) Na_3PO_4 . Photographs of DW_{20d} aqueous dispersions with
612 NaCl (g) in a liquid state ($\phi = 0.36\%$) and (h) above the glass transition ($\phi = 0.94\%$). The latter
613 does not flow upon tube reversal.

614
615 **Figure 3.** Polarized optical microscopy observations of DW_{20d} aqueous dispersions prepared at
616 different volume fractions ϕ with NaCl ($IS = 10^{-3} \text{ mol.L}^{-1}$). The images on the right are taken with
617 the addition of a retardation filter (λ -plate, 530 nm). The white arrows and the red line indicate
618 the orientation of the polarizers and the slow axis of the retardation filter, respectively.

619
620 **Figure 4.** Effect of the electrolyte type on optical textures of (a-c) DW_{5d} ($\phi \sim 0.4\%$) and (d-f)
621 DW_{20d} ($\phi \sim 0.35\%$) aqueous dispersions. (a,d) NaCl; (b,e) Na_2SO_4 ; (c,f) Na_3PO_4 .

622
623 **Figure 5.** Evolution of the scattering intensity $I(Q)$ as a function of the scattering vector Q for (a)
624 DW_{5d} and (b) DW_{20d} dispersions prepared in different salts (NaCl, Na_2SO_4 and Na_3PO_4) at a
625 fixed volume fraction of $\phi = 0.72\%$ and $\phi = 0.56\%$ respectively.

626

627 **Figure 6.** Evolution of the structure factors as a function of the scattering vector Q for DW_{5d}
628 (*left*) and DW_{20d} (*right*) dispersions at various volume fractions ϕ with (a,b) NaCl; (c,d) Na₂SO₄
629 and (e,f) Na₃PO₄ electrolytes.

630
631 **Figure 7.** (a) Evolution of the interparticle distance deduced from SAXS curves as a function of
632 $\phi^{-0.5}$. The dotted line corresponds to the model described in Eq. (2). (b) Interparticle distance as a
633 function of Ge-DWINTs volume fraction ϕ . The lines correspond to the fit calculated from Eq.
634 (3).

635
636 **Figure 8.** Energy of interaction per nm as a function of the interparticle distance for aqueous
637 dispersions of imogolite nanotubes. Calculations are performed at room temperature for an ionic
638 strength $I = 10^{-3}$ mol.L⁻¹, a surface potential $\psi_0 = 50$ mV, a Hamaker constant $A = 6.7 \times 10^{-20}$ J
639 and a nanotube radius $a = 2.2$ nm (see text for details).

640
641 **Figure 9.** Phase diagram as a function of Ge-DWINTs volume fraction ϕ for DW_{5d} and DW_{20d}
642 with NaCl, Na₂SO₄ and Na₃PO₄ salts. The dotted lines between the different regimes are to guide
643 the eyes.

644

645

Supplementary material

646 **Colloidal phase behavior of high aspect ratio clay nanotubes**

647 **in symmetric and asymmetric electrolytes**

648

649 Claire HOTTON^{a,*}, Léna LE ROUX^a, Claire GOLDMANN^a, Stéphan ROUZIÈRE^a,

650 Pascale LAUNOIS^a, Thomas BIZIEN^b, Erwan PAINEAU^{a,*}

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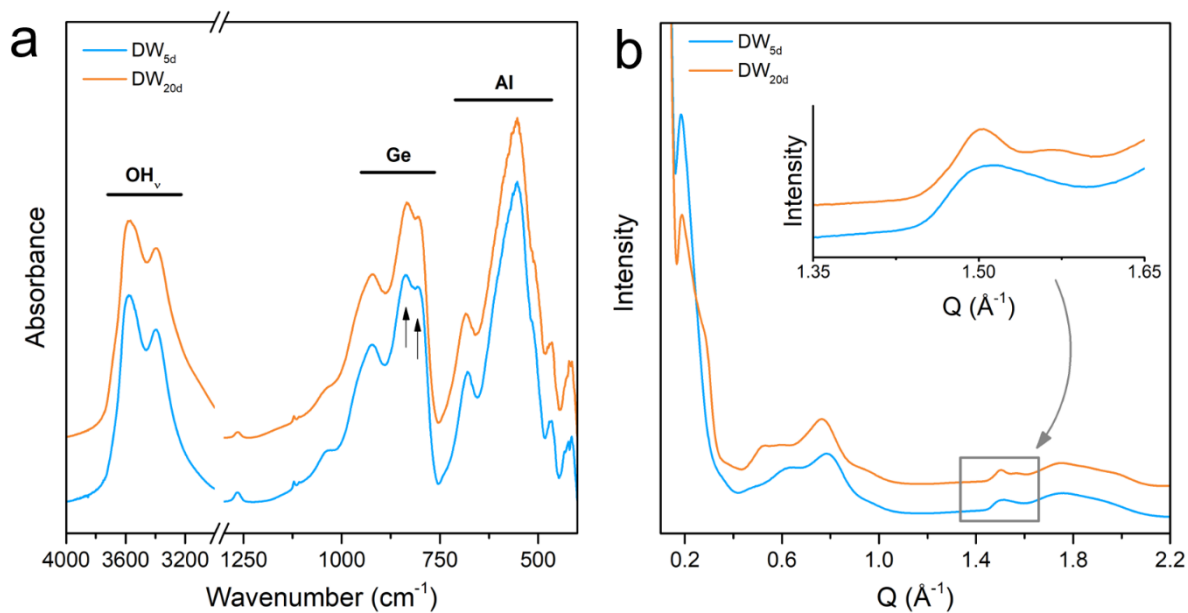
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653 1. Characterization of Ge-DWINTs batches

654
655 Fourier Transform Infrared (FTIR) spectroscopy was realized on KBr pressed pellets
656 containing ~ 1%wt of Ge-DWINTs powder. Acquisitions were performed with a Nicolet
657 iS50 FTIR spectrometer equipped with a KBr beamsplitter and a DTGS/KBr detector.
658 The resulting FTIR spectra correspond to the average of 64 scans at a resolution of 4
659 cm^{-1} . The obtained spectra (Figure S1a) display the vibrations of imogolite nanotubes at
660 910 cm^{-1} and the characteristic doublet at $830/805 \text{ cm}^{-1}$ related to the local structure of
661 aluminogermanate imogolite nanotubes. These vibrations are assigned to Ge-O
662 stretching in isolated GeO_4 structures, while the absorption bands at 690, 555 and 420
663 cm^{-1} are related to Al-O vibrations in the INT structure.^{S1,S2} In addition, FTIR curves
664 present two broad peaks at 3580 and 3400 cm^{-1} that are related to O-H stretching (OHv)
665 of outer and inner hydroxyl groups.

666 Characterization of synthetic Ge-DWINTs was completed by laboratory X-ray scattering
667 (XRS) on the MORPHEUS platform at Laboratoire de Physique des Solides.
668 Experiments were realized on a rotating anode generator (RU H3R, Rigaku Corp.,
669 Japan) operating at the $\text{CuK}\alpha$ wavelength delivered by Osmic optics. Powder samples
670 were packed in borosilicate glass capillaries (WJM Glas/Müller GmbH, Germany) and
671 placed at a sample-to-detector distance of 250 mm. The scattering signals were
672 collected on a two-dimensional mar345 image plate detector (marXperts GmbH,
673 Germany) with a $150 \mu\text{m}$ pixel size. Angular integration of the 2D patterns were
674 performed to obtain the dependence of the scattered intensity $I(Q)$ presented in Figure
675 S1b. The diffractograms show large oscillations related to the form factor of a tubular
676 structure as detailed previously.^{S3} In particular, the enhanced intensity between 0.4 and
677 0.9 \AA^{-1} is characteristic of the mean inter-wall distance in a double-walled nanotube.^{S4,S5}
678 The 002 asymmetric peak around 1.5 \AA^{-1} is a signature of the one-dimensional
679 periodicity along the nanotube axis,^{S6} the period being equal to $\sim 8.5 \text{ \AA}$.

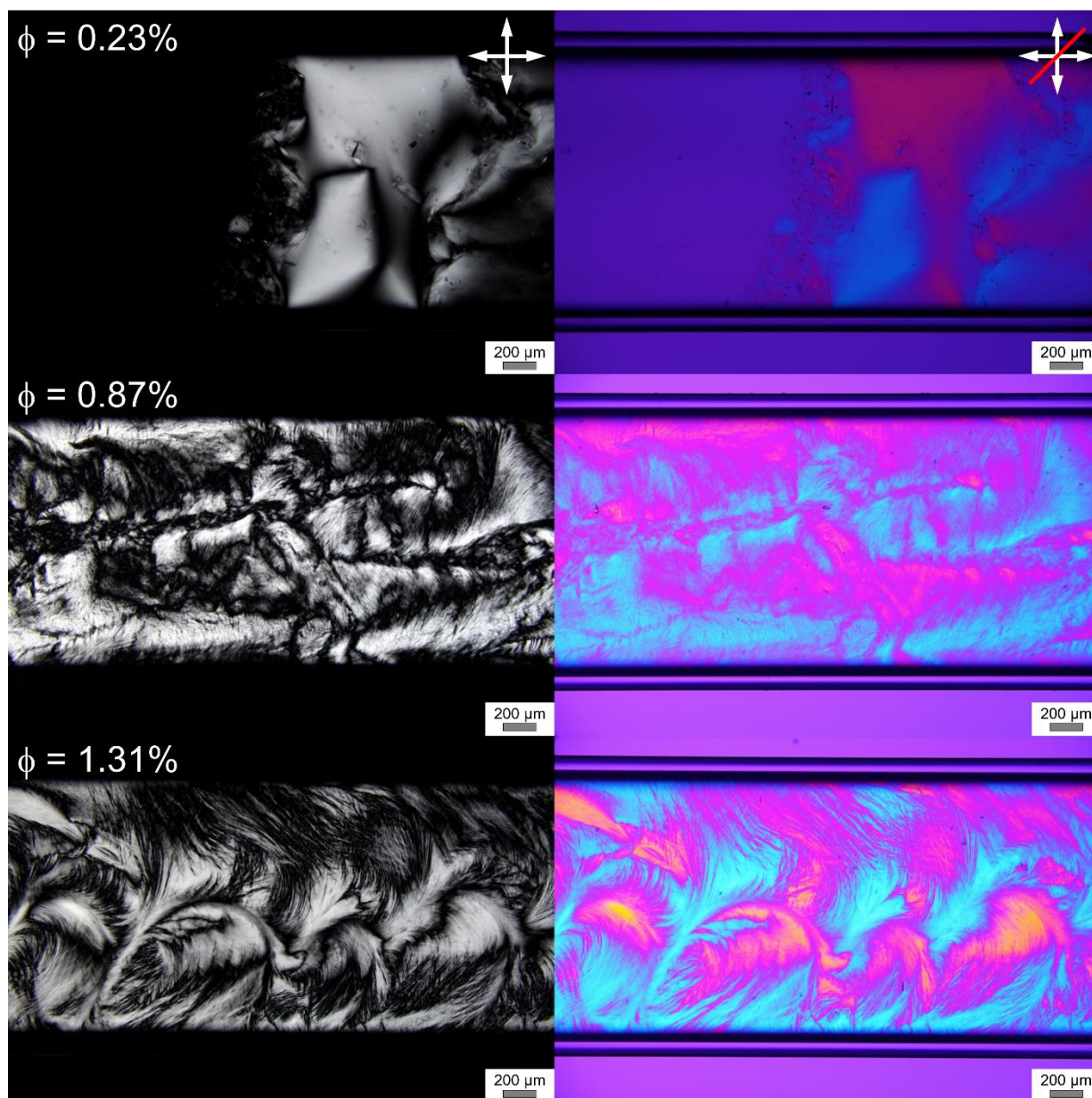
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 682 **Fig. S1.** (a) FTIR spectra and (b) X-ray scattering patterns of Ge-DWINTs feedstocks.
 683 The curves are translated for the sake of clarity. The two black arrows in panel (a)
 684 highlight the characteristic doublet at 830/805 cm⁻¹ related to the local structure of
 685 aluminogermanate imogolite nanotubes. The inset in panel (b) is an enlarge view around
 686 the 002 asymmetric peak characteristic of the nanotube periodicity.

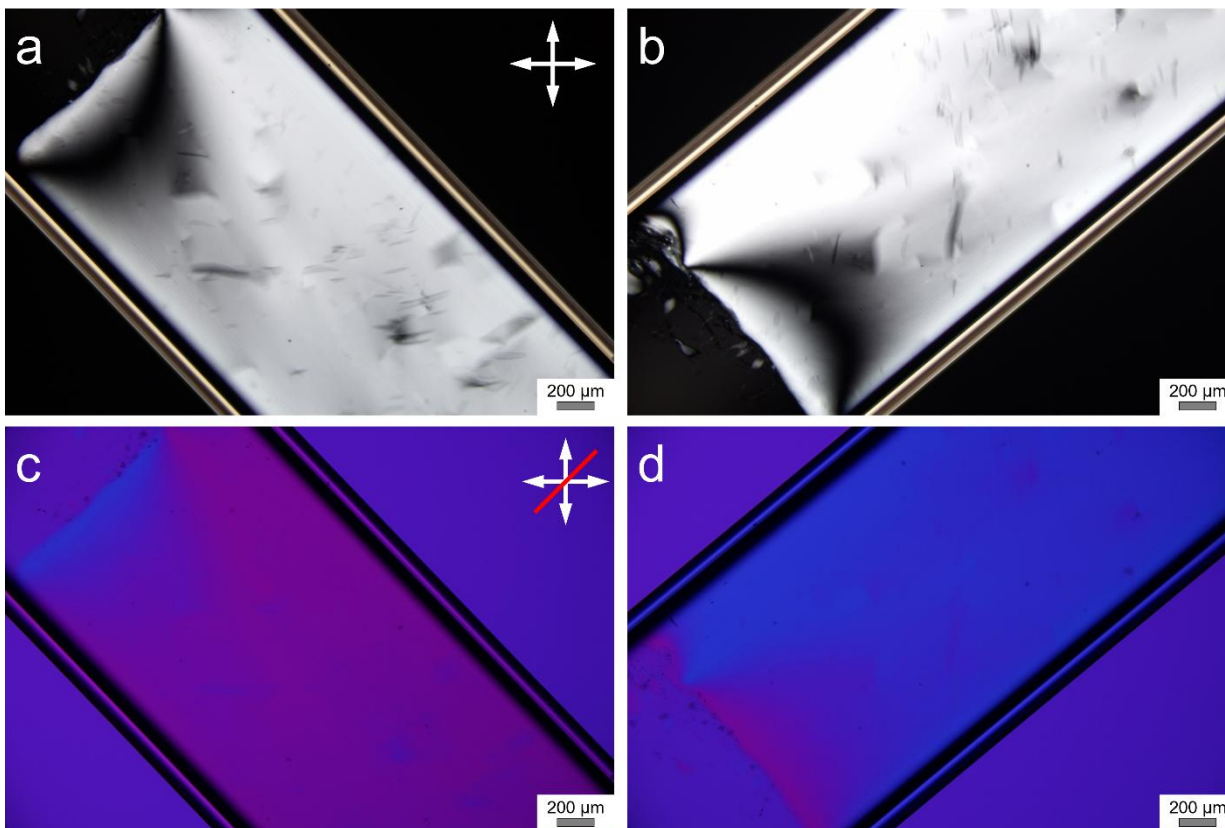
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2. Polarized optical microscopy



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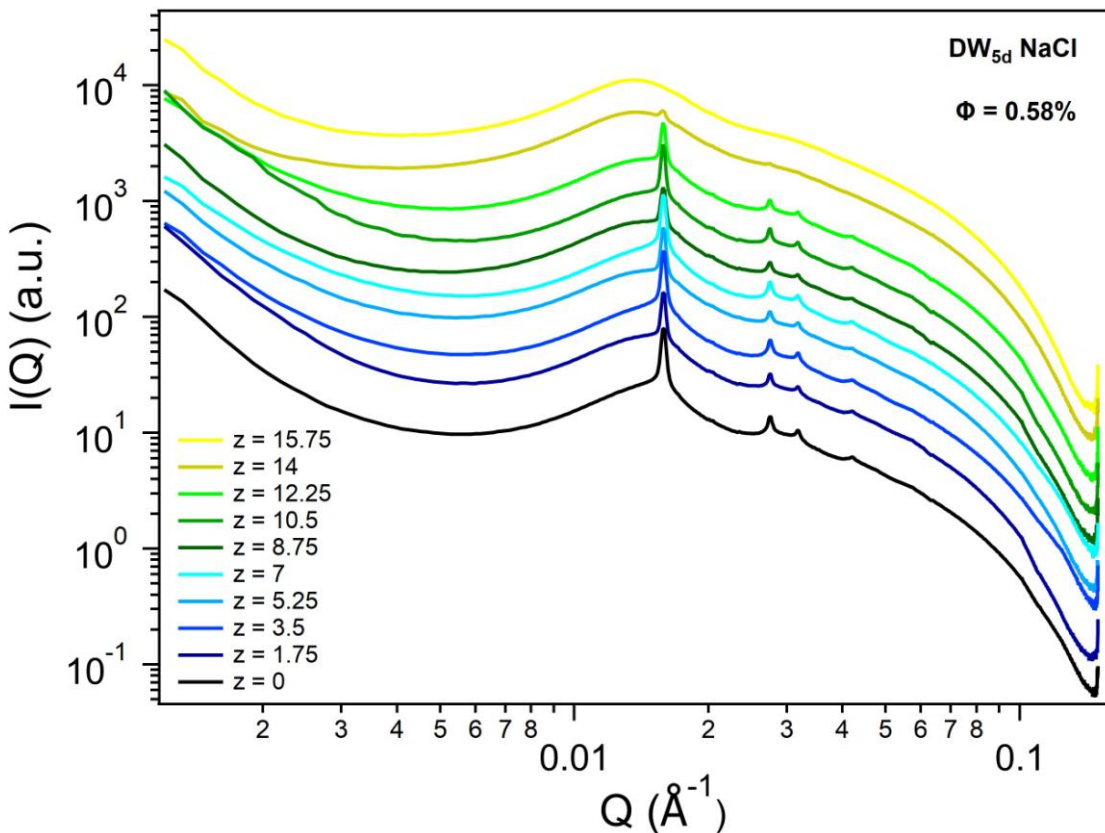
690 **Fig. S2.** Polarized optical microscopy observations of DW_{5d} aqueous dispersions
691 prepared at different volume fractions ϕ with NaCl ($I_S = 10^{-3} \text{ mol.L}^{-1}$). The images are
692 taken (*left*) without and (*right*) with the addition of a retardation filter (λ -plate, 530 nm).
693 The white arrows and the red line indicate the orientation of the polarizers and the slow
694 axis of the retardation filter, respectively.
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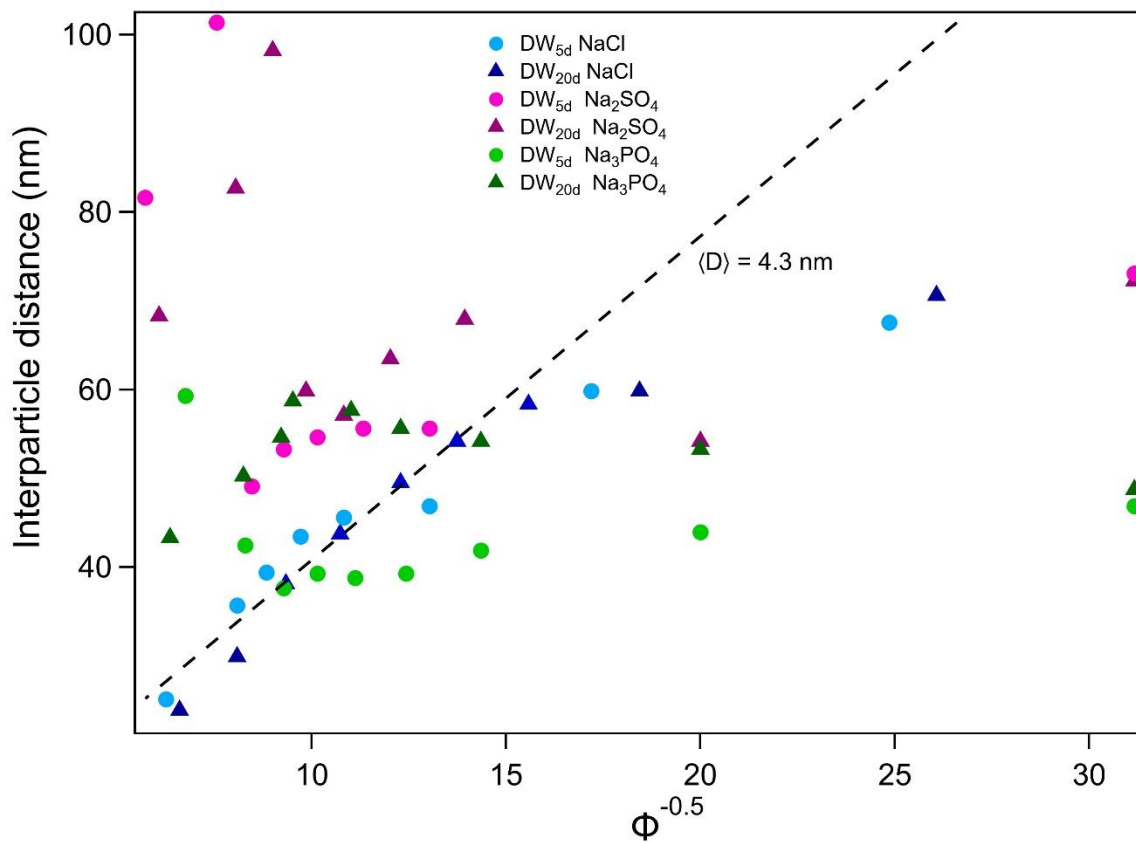
Fig. S3. Optical textures in polarized light microscopy of DW_{20d} aqueous dispersions ($\phi = 0.1\%$, $[NaCl] = 10^{-3} \text{ mol.L}^{-1}$) without (a,b) and with (c,d) a retardation filter (λ -plate, 530 nm). The sample is tilted by 45° clockwise (a,c) and counter-clockwise (b,d). The white arrows and the red line indicate the orientation of the polarizers and the slow axis of the retardation filter, respectively.

705 **3. Scanning along the capillary by Small Angle X-ray Scattering**
706



707 **Fig. S4.** Evolution of the scattering intensity $I(Q)$ as a function of the scattering vector Q
708 along the capillary (from top at $z = 15.75$ mm corresponding to the yellow curve to
709 bottom at $z = 0$ mm corresponding to the black curve) of a DW_{5d} dispersion prepared in
710 NaCl at a volume fraction of 0.58%. All curves have been shifted vertically for the sake
711 of clarity.
712
713
714

715 **4. Swelling laws**
 716



717
 718 **Fig. S5.** Evolution of the interparticle distance with $\phi^{-0.5}$ for aqueous dispersions of DW_{5d}
 719 (circles) and DW_{20d} (triangles) as a function of the electrolytes ($IS = 10^{-3} \text{ mol.L}^{-1}$). The
 720 dashed line corresponds to the packing of the nanotubes assuming a 2D hexagonal
 721 configuration and a nanotube diameter of 4.3 nm.
 722

5. DLVO calculations

For a symmetric electrolyte such as NaCl, it is possible to calculate the energy of interactions between two charged cylindrical nanoparticles through the DLVO theory. This corresponds to the sum of repulsive electrostatic forces (V_R) due to the diffuse double layer of ions and the van der Waals attractive energy (V_A). Since the nanotubes present preferential orientation, we can assume in a first approximation that they lie parallel. In this case, the repulsive energy for charged cylinders of aspect ratio $L/2a$ is given by the expression^{S7}:

$$V_R = 64\pi^{1/2}nkT \left(\tanh\left(\frac{e\psi_0}{4kT}\right) \right)^2 L \frac{(\kappa a)^{1/2}}{\kappa^2} e^{-\kappa(\langle d \rangle - \langle 2a \rangle)} \quad (SI1)$$

with n the number density of ions in the suspension, e the proton charge and ψ_0 the particle surface potential. We take $\psi_0 = 50$ mV deduced from previous zeta-potential measurements on DWINTs.^{S2} κ is the inverse of the Debye screening length of the diffuse double layer, which for 1:1 electrolytes is $\sqrt{I}/0.304 \times 10^{-9}$ (nm⁻¹). For the van der Waals attractive energy, the expression depends on the interparticle distance $\langle d \rangle$. For short values (typically $(\langle d \rangle - \langle 2a \rangle) \ll a$), the attractive term is:

$$V_A = -\frac{A}{24} \frac{L}{a} \left(\frac{a}{\langle d \rangle - \langle 2a \rangle} \right)^{\frac{3}{2}} \left(1 - \frac{9}{8} \frac{\langle d \rangle - \langle 2a \rangle}{a} \right) \quad (SI2)$$

with A the Hamaker constant. For larger interparticle distances, the expression of V_A becomes:

$$V_A = -\frac{3\pi}{8} A \frac{L}{a} a^5 U_5 \quad (SI3)$$

where U_5 is a function which depends on the cylinder radius and the distance $\langle d \rangle$ between the cylinder axes and which can be developed in a series of $\frac{a}{\langle d \rangle}$ as detailed in ref. [S7]. The Hamaker constant of imogolite nanotubes being never estimated, we have used the value reported for AlO(OH) nanorods ($A = 6.7 \times 10^{-20}$ J),^{S8} assuming the aluminum outer surface of imogolite nanotubes to be close to boehmite. Similar values of V_A are obtained from eq. (SI2) and (SI3) for $\langle d \rangle - \langle 2a \rangle = a/2$, which is the crossover value chosen for using one or the other equation to calculate the total energy of interaction $V = V_R + V_A$.

750 **6. Additional references**

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