



**HAL**  
open science

## Colloidal phase behavior of high aspect ratio clay nanotubes in symmetric and asymmetric electrolytes

Claire Hotton, Léna Le Roux, Claire Goldmann, Stéphan Rouzière, Pascale Launois, Thomas Bizien, Erwan Paineau

### ► To cite this version:

Claire Hotton, Léna Le Roux, Claire Goldmann, Stéphan Rouzière, Pascale Launois, et al.. Colloidal phase behavior of high aspect ratio clay nanotubes in symmetric and asymmetric electrolytes. *Journal of Colloid and Interface Science*, 2024, 664, pp.857-867. 10.1016/j.jcis.2024.03.046 . hal-04507544

**HAL Id: hal-04507544**

**<https://hal.science/hal-04507544v1>**

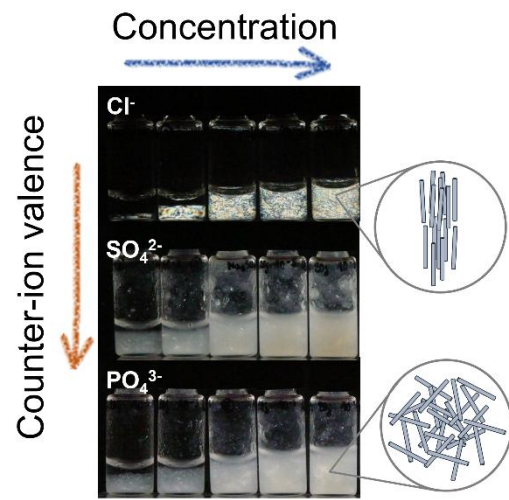
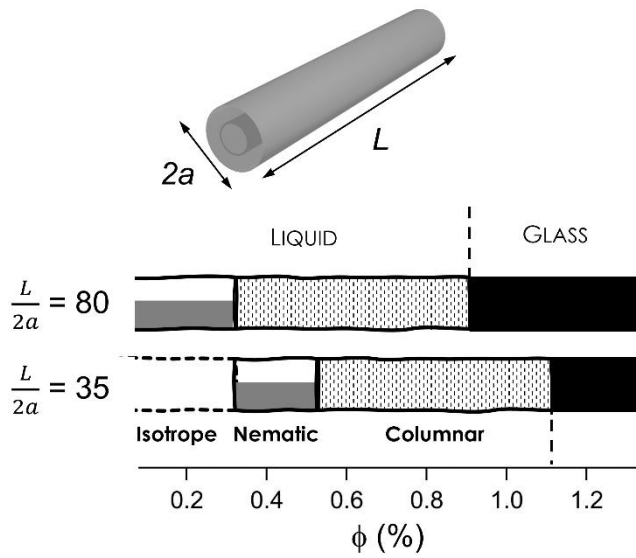
Submitted on 16 Mar 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Graphical abstract:**

2



3

4

5

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

8  
9 Claire HOTTON<sup>a,\*</sup>, Léna LE ROUX<sup>a</sup>, Claire GOLDMANN<sup>a</sup>, Stéphan ROUZIÈRE<sup>a</sup>, Pascale  
10 LAUNOIS<sup>a</sup>, Thomas BIZIEN<sup>b</sup>, Erwan PAINEAU<sup>a,\*</sup>

11  
12 <sup>a</sup> Université Paris-Saclay, CNRS, Laboratoire de Physique des Solides, Orsay, 91405, France

13 <sup>b</sup> Synchrotron SOLEIL, L'Orme des Merisiers, 91192 Gif-sur-Yvette Cedex, France

14  
15 \* Corresponding authors:  
16 Laboratoire de Physique des Solides, Université Paris-Saclay, Bat.510, 1 rue Nicolas Appert,  
17 91405 Orsay, France.  
18 [claire.hotton@universite-paris-saclay.fr](mailto:claire.hotton@universite-paris-saclay.fr). Phone: +33 (0) 1 69 15 53 94  
19 [erwan-nicolas.paineau@universite-paris-saclay.fr](mailto:erwan-nicolas.paineau@universite-paris-saclay.fr). Phone: +33 (0) 1 69 15 60 51

20

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<sup>-1</sup> 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<sup>-1</sup>) were prepared  
117 with NaCl, Na<sub>2</sub>SO<sub>4</sub> or Na<sub>3</sub>PO<sub>4</sub> electrolytes. The value of the imposed strength was chosen based  
118 on previous studies showing that below  $10^{-2}$  mol.L<sup>-1</sup>, 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<sup>-1</sup>, 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<sub>5d</sub> and DW<sub>20d</sub> 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<sup>-1</sup> [51]. Transmission  
137 electron microscopy (TEM) experiments were performed to determine the length distribution of  
138 the nanotubes. For both DW<sub>5d</sub> and DW<sub>20d</sub>, a dispersion was prepared at 1 mg.L<sup>-1</sup> 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<sub>5d</sub> and DW<sub>20d</sub> stocks in a 2L beaker containing a  
145 polyethylene glycol solution (M<sub>w</sub> = 20000 g.mol<sup>-1</sup>, C = 20 g.L<sup>-1</sup>). An appropriate amount of  
146 NaCl, Na<sub>2</sub>SO<sub>4</sub> or Na<sub>3</sub>PO<sub>4</sub> salts was added to keep a constant ionic strength *I*, fixed at 10<sup>-3</sup> M,  
147 according to:

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

148 with *c<sub>i</sub>* the molar concentration of ions, *z<sub>i</sub>* 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  $\phi$  ( $\phi = C/\rho_{INT}$  with *C* the solid concentration of Ge-DWINTs and  
151  $\rho_{INT}$  the density of a nanotube taken as 3.6 g.cm<sup>-3</sup> [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<sup>-3</sup> 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)**

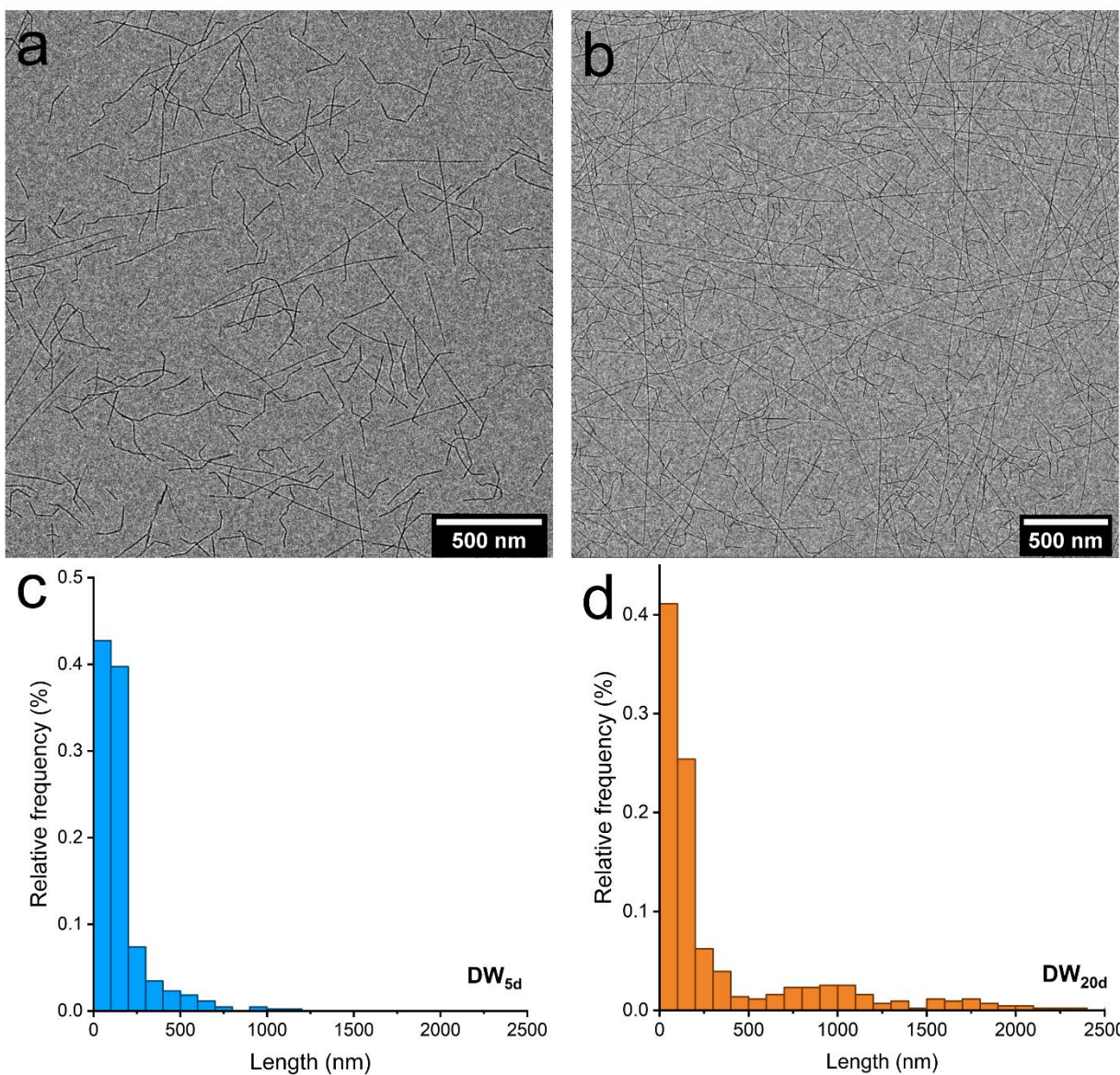
162 Synchrotron-based SAXS experiments were realized at the SWING beamline (SOLEIL  
163 synchrotron, Saint-Aubin, France) and a fixed wavelength  $\lambda = 1.0332 \text{ \AA}$ . The scattering patterns  
164 were collected on a two-dimensional detector (Eiger 4M, Dectris Ltd., Switzerland) placed at 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  $2\theta$  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<sub>20d</sub>. 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<sub>5d</sub> and 350 nm for  
182 DW<sub>20d</sub>. Moreover, the latter presents a significant proportion of nanotubes with length around  
183 900 nm.

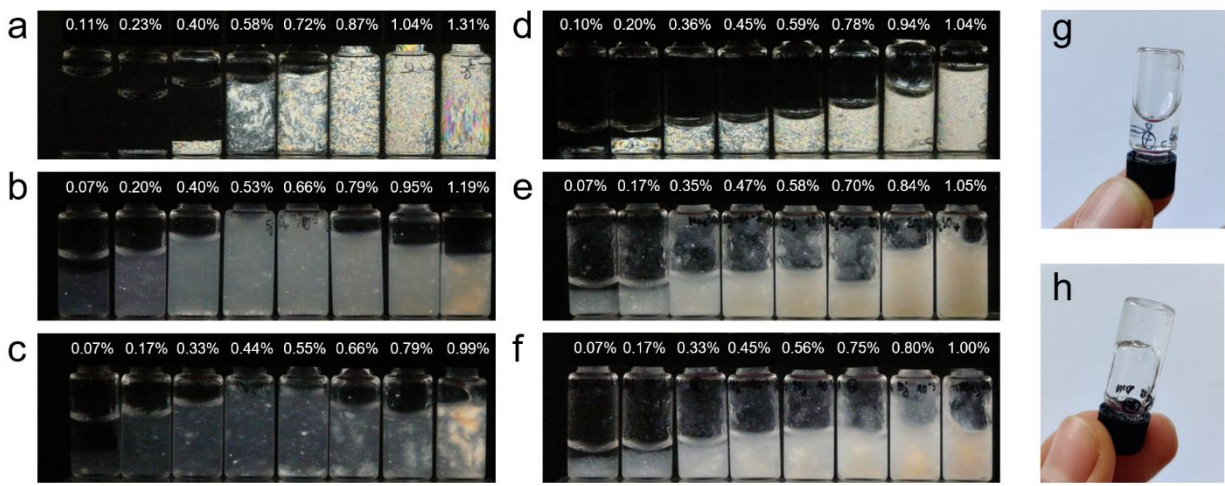


184

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<sub>5d</sub>  
187 and (d) DW<sub>20d</sub>.

### 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 Na<sub>2</sub>SO<sub>4</sub> or Na<sub>3</sub>PO<sub>4</sub> 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<sup>-1</sup>) controlled  
197 by these different salts (NaCl, Na<sub>2</sub>SO<sub>4</sub> and Na<sub>3</sub>PO<sub>4</sub>) 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  $\phi$  and electrolytes ( $IS = 10^{-3}$   
 205  $\text{mol.L}^{-1}$ ). (a,d) NaCl; (b,e)  $\text{Na}_2\text{SO}_4$ ; (c,f)  $\text{Na}_3\text{PO}_4$ . 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

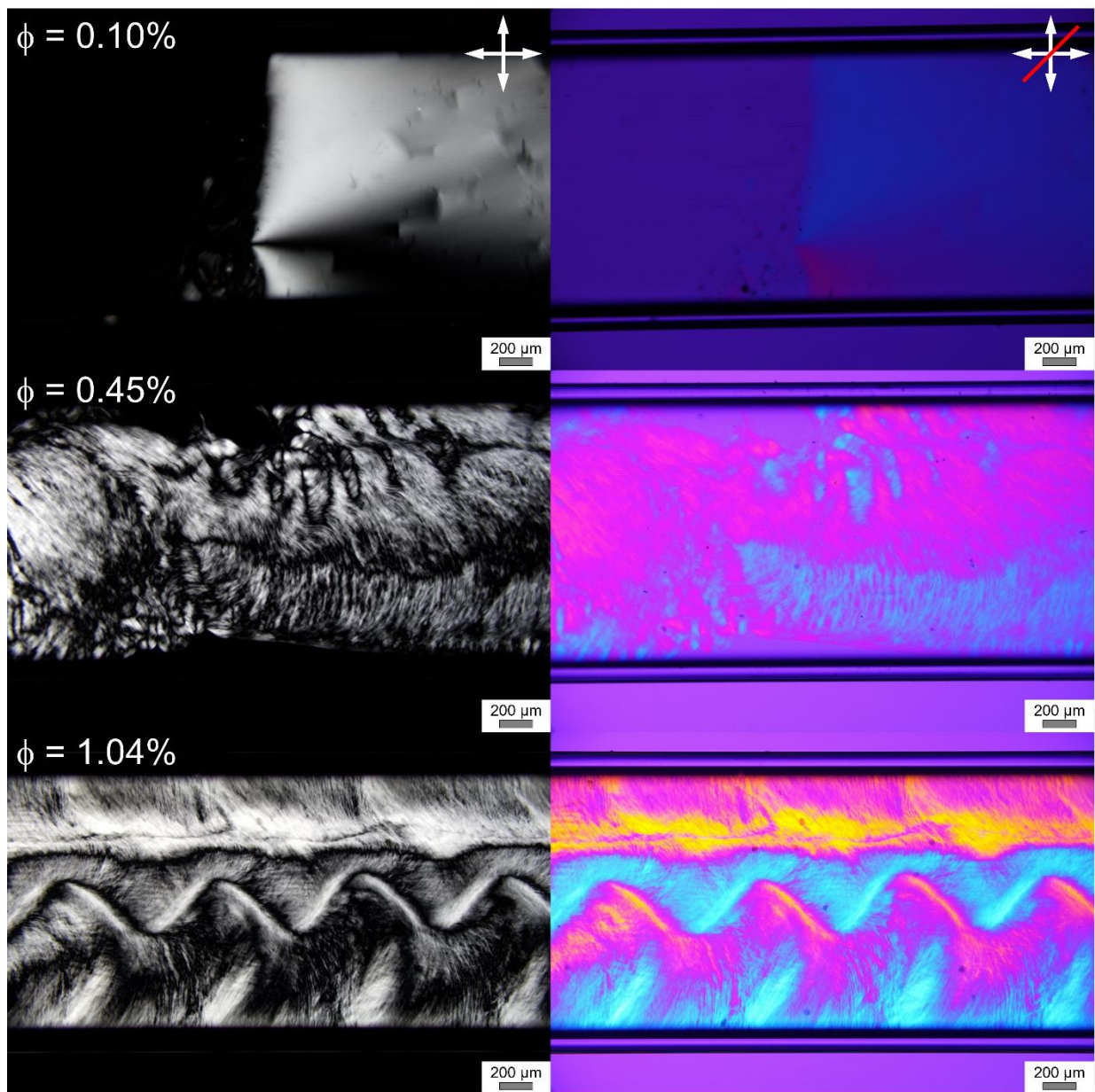
219 have a preferred orientation. They can therefore be considered as a glass-like state, where the  
220 slowing of the nanotubes dynamics is due exclusively to excluded volume effects [6].

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<sub>5d</sub> and  
231 DW<sub>20d</sub> 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<sub>20d</sub> 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  $\lambda$ -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

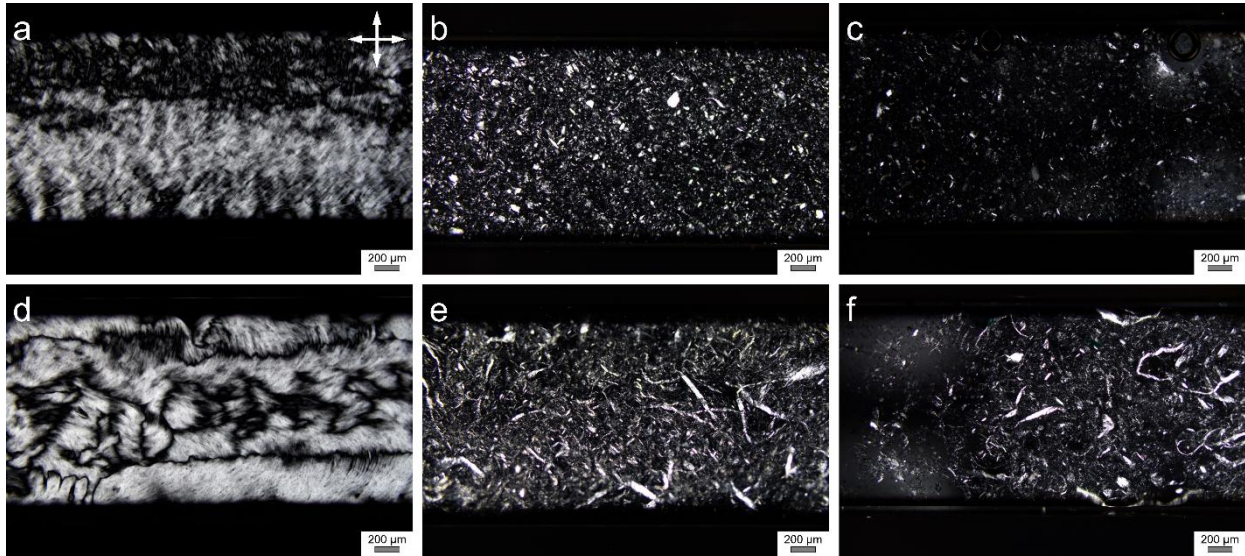
253 **Figure 3.** Polarized optical microscopy observations of  $DW_{20d}$  aqueous dispersions prepared at

254 different volume fractions  $\phi$  with NaCl ( $IS = 10^{-3} \text{ mol.L}^{-1}$ ). The images on the right are taken with

255 the addition of a retardation filter ( $\lambda$ -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.





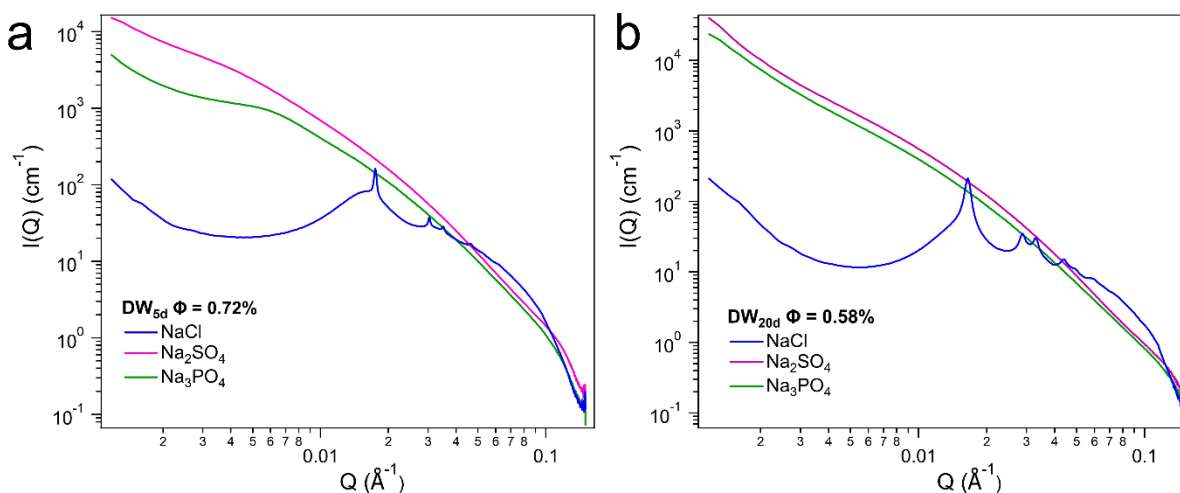
257  
 258 **Figure 4.** Effect of the electrolyte type on optical textures of (a-c) DW<sub>5d</sub> ( $\phi \sim 0.4\%$ ) and (d-f)  
 259 DW<sub>20d</sub> ( $\phi \sim 0.35\%$ ) aqueous dispersions. (a,d) NaCl; (b,e) Na<sub>2</sub>SO<sub>4</sub>; (c,f) Na<sub>3</sub>PO<sub>4</sub>.

### 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.

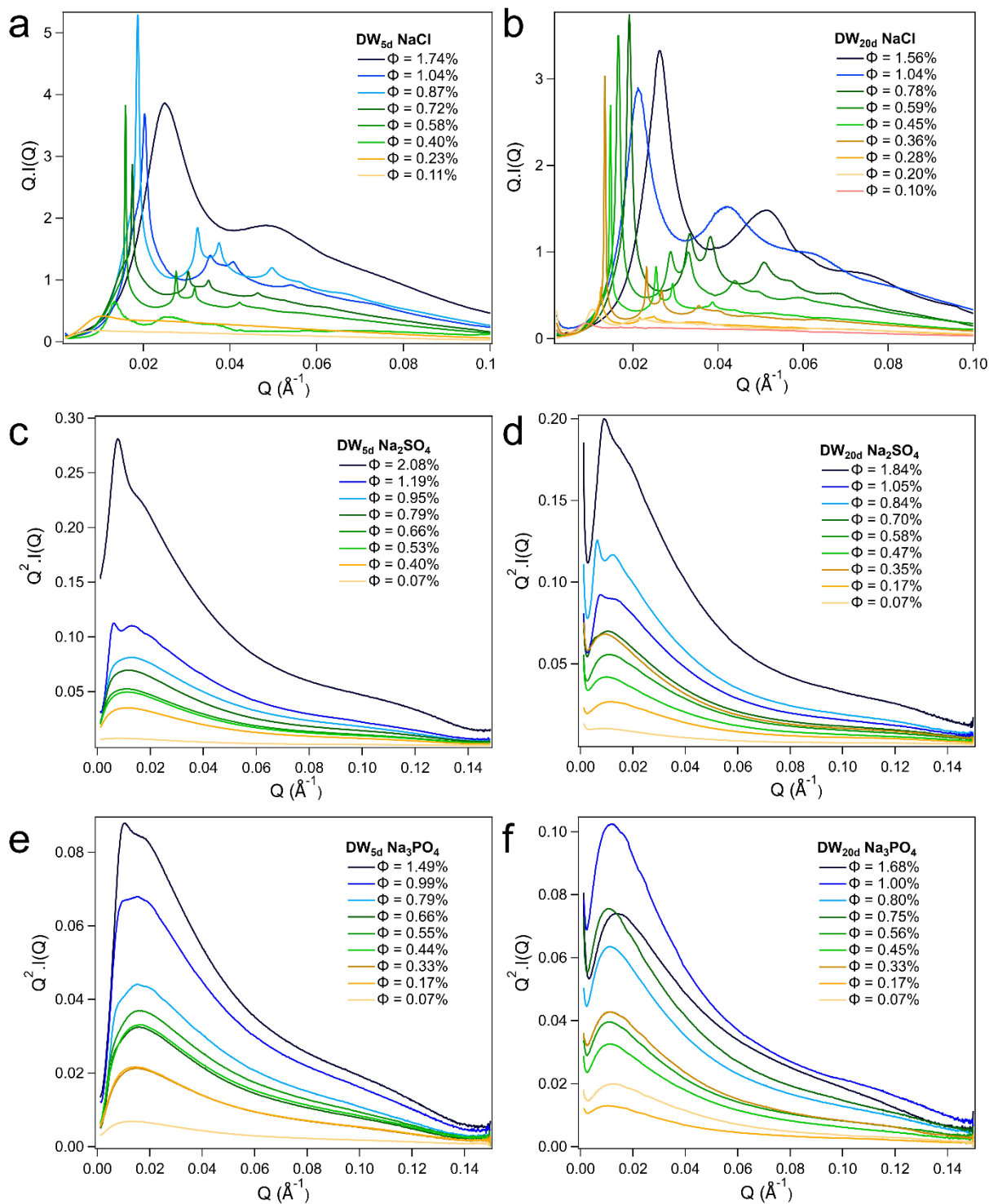
267 Scattering intensities are first analyzed at a fixed volume fraction, chosen to compare dispersions  
 268 in multivalent salts with dispersions in NaCl presenting a liquid-crystal organization. As shown  
 269 in Figure 5, scattering intensities differ significantly between dispersions with monovalent 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<sub>H</sub>) phase [34,40,53].

273 In the middle- $Q$  region  $[0.01-0.1 \text{ \AA}^{-1}]$ , 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.

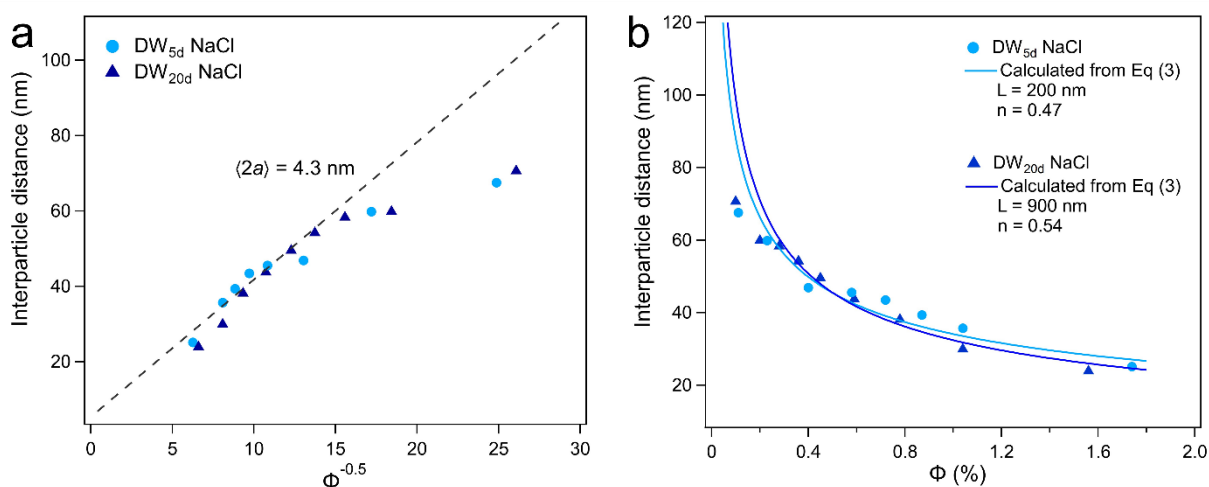


286  
 287 **Figure 6.** Evolution of the structure factors as a function of the scattering vector  $Q$  for  $DW_{5d}$   
 288 (*left*) and  $DW_{20d}$  (*right*) dispersions at various volume fractions  $\phi$  with (a,b) NaCl; (c,d)  $Na_2SO_4$   
 289 and (e,f)  $Na_3PO_4$  electrolytes.

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<sub>H</sub>) 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  $\gamma$  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  $\phi$ . 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 
$$\langle d \rangle = \left( \frac{\pi\sqrt{3}}{8} \right)^{\frac{1}{2}} \langle 2a \rangle \phi^{-0.5} \quad (2)$$

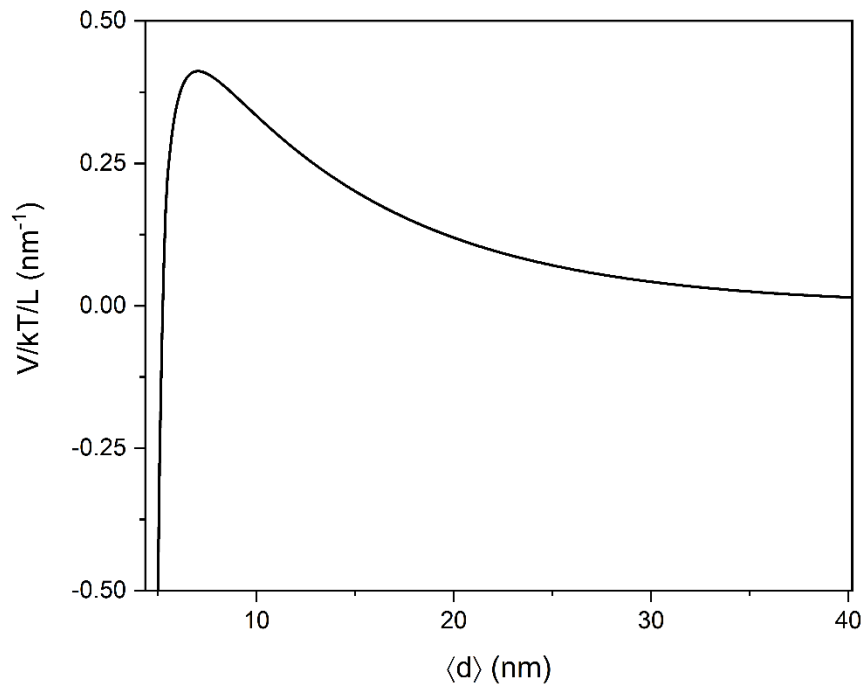
331 By using eq. (2), we find a value of  $\langle 2a \rangle \sim 4.3$  nm, which is in good agreement with the outer  
 332 diameter of Ge-DWINTs as determined previously [40]. If we perform the same analysis on  
 333 dispersions prepared with divalent or trivalent electrolytes, the position of the 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  $\phi_{eff}$  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  $\phi_{eff}^*$  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<sub>5d</sub> and DW<sub>20d</sub>, 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.



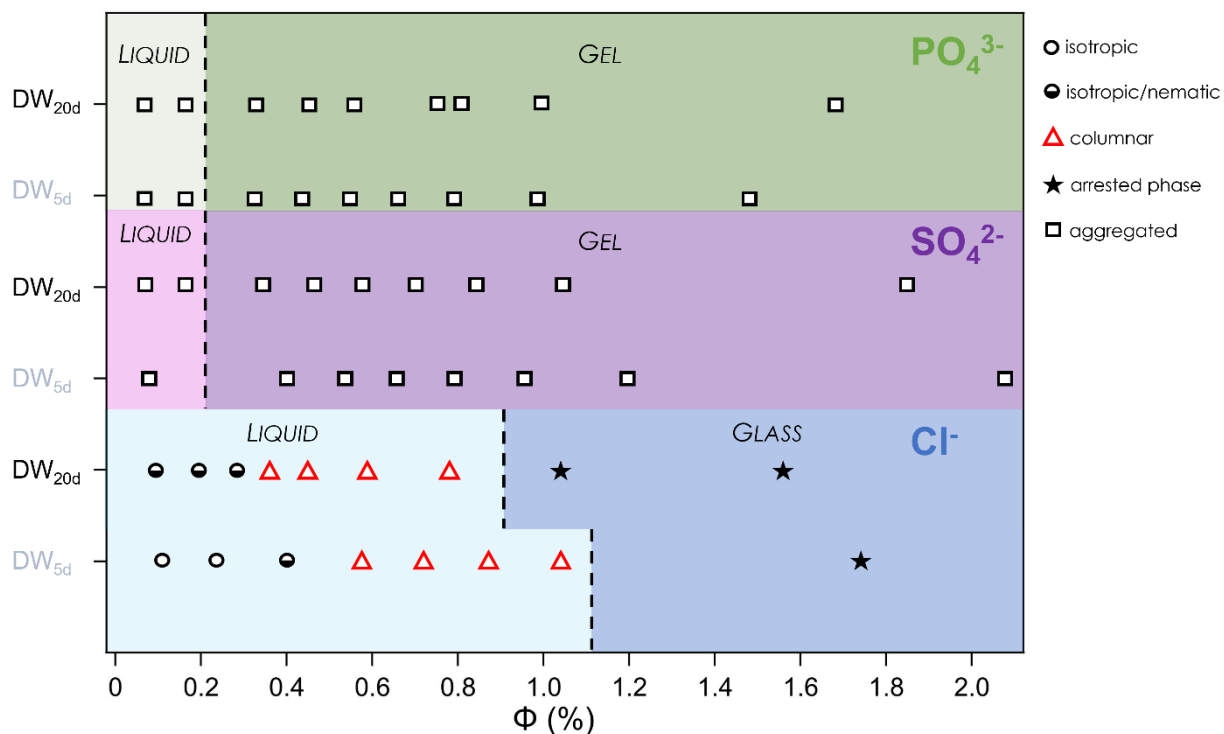
362  
 363 **Figure 8.** Energy of interaction per nm as a function of the interparticle distance for aqueous  
 364 dispersions of imogolite nanotubes. Calculations are performed at room temperature for an ionic  
 365 strength  $I = 10^{-3}$  mol.L $^{-1}$ , a surface potential  $\psi_0 = 50$  mV, 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  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_3\text{PO}_4$  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  $\phi$  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<sup>-1</sup>). We demonstrated that divalent (SO<sub>4</sub><sup>2-</sup>) or trivalent (PO<sub>4</sub><sup>3-</sup>) 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].

## 419 **5. Acknowledgments**

420 The authors acknowledge the SOLEIL synchrotron for allocating beamtime on the SWING  
421 beamline (BAG proposal 20221057) and the MORPHEUS platform (LPS, Orsay) for X-ray  
422 scattering experiments. This work had benefited from an Investissements d'Avenir grant from  
423 Labex PALM (ANR-10-LABX-0039-PALM) and from Imagerie-Gif core facility supported by  
424 l'Agence Nationale de la Recherche (ANR-11-EQPX-0029/Morphoscope; ANR-10-INBS-  
425 04/FranceBioImaging; ANR-11-IDEX-0003-02/Saclay Plant Sciences).

## 426 **References**

- 427 [1] W.J. Stark, P.R. Stoessel, W. Wohlleben, A. Hafner, Industrial applications of nanoparticles,  
428 Chem. Soc. Rev. 44 (2015) 5793–5805.
- 429 [2] M.J. Mitchell, M.M. Billingsley, R.M. Haley, M.E. Wechsler, N.A. Peppas, R. Langer,  
430 Engineering precision nanoparticles for drug delivery, Nat. Rev. Drug Discov. 20 (2021) 101–  
431 124.
- 432 [3] L. Onsager, The effects of shape on the interaction of colloidal particles, Ann. N. Y. Acad. Sci.  
433 51 (1949) 627–659.
- 434 [4] H.H. Wensink, G.J. Vroege, Isotropic-nematic phase behavior of length-polydisperse hard  
435 rods, J. Chem. Phys. 119 (2003) 6868–6882. <https://doi.org/10.1063/1.1599277>.
- 436 [5] D. Frenkel, Order through entropy, Nat. Mater. 14 (2015) 9–12.
- 437 [6] M.J. Solomon, P.T. Spicer, Microstructural regimes of colloidal rod suspensions, gels, and  
438 glasses, Soft Matter 6 (2010) 1391–1400.
- 439 [7] N. Miyamoto, T. Nakato, Liquid crystalline inorganic nanosheet colloids derived from layered  
440 materials, Isr. J. Chem. 52 (2012) 881–894.
- 441 [8] H.N.W. Lekkerkerker, G.J. Vroege, Liquid crystal phase transitions in suspensions of mineral  
442 colloids: new life from old roots, Philos. Trans. R. Soc. Math. Phys. Eng. Sci. 371 (2013)  
443 20120263.
- 444 [9] I. Dierking, S. Al-Zangana, Lyotropic liquid crystal phases from anisotropic nanomaterials,  
445 Nanomaterials 7 (2017) 305.
- 446 [10] S.P. Sasikala, J. Lim, I.H. Kim, H.J. Jung, T. Yun, T.H. Han, S.O. Kim, Graphene oxide liquid  
447 crystals: a frontier 2D soft material for graphene-based functional materials, Chem. Soc.  
448 Rev. 47 (2018) 6013–6045.
- 449 [11] P. Davidson, C. Penisson, D. Constantin, J.-C.P. Gabriel, Isotropic, nematic, and lamellar  
450 phases in colloidal suspensions of nanosheets, Proc. Natl. Acad. Sci. 115 (2018) 6662–6667.

- 451 [12] L.J. Michot, I. Bihannic, S. Maddi, S.S. Funari, C. Baravian, P. Levitz, P. Davidson, Liquid–  
452 crystalline aqueous clay suspensions, *Proc. Natl. Acad. Sci.* 103 (2006) 16101–16104.
- 453 [13] L.J. Michot, E. Paineau, I. Bihannic, S. Maddi, J.F.L. Duval, C. Baravian, P. Davidson, P.  
454 Levitz, Isotropic/nematic and sol/gel transitions in aqueous suspensions of size selected  
455 nontronite NAul, *Clay Miner.* 48 (2013) 663–685.  
456 <https://doi.org/10.1180/claymin.2013.048.5.01>.
- 457 [14] E. Paineau, K. Antonova, C. Baravian, I. Bihannic, P. Davidson, I. Dozov, M. Imperor-Clerc,  
458 P. Levitz, A. Madsen, F. Meneau, L.J. Michot, Liquid-Crystalline Nematic Phase in Aqueous  
459 Suspensions of a Disk-Shaped Natural Beidellite Clay, *J. Phys. Chem. B* 113 (2009) 15858–  
460 15869.
- 461 [15] K. El Rifaii, H.H. Wensink, I. Dozov, T. Bizien, L.J. Michot, J.-C.P. Gabriel, J. Breu, P.  
462 Davidson, Do aqueous suspensions of smectite clays form a smectic liquid-crystalline  
463 phase?, *Langmuir* 38 (2022) 14563–14573.
- 464 [16] O. Khoruzhenko, D.R. Wagner, S. Mangelsen, M. Dulle, S. Förster, S. Rosenfeldt, V.  
465 Dudko, K. Ottermann, G. Papastavrou, W. Bensch, Colloidally stable, magnetoresponse  
466 liquid crystals based on clay nanosheets, *J. Mater. Chem. C* 9 (2021) 12732–12740.
- 467 [17] L.J. Michot, I. Bihannic, K. Porsch, S. Maddi, C. Baravian, J. Mougel, P. Levitz, Phase  
468 diagrams of Wyoming Na-montmorillonite clay. Influence of particle anisotropy, *Langmuir*  
469 20 (2004) 10829–10837.
- 470 [18] D. Yamaguchi, N. Miyamoto, T. Fujita, T. Nakato, S. Koizumi, N. Ohta, N. Yagi, T.  
471 Hashimoto, Aspect-ratio-dependent phase transitions and concentration fluctuations in  
472 aqueous colloidal dispersions of charged platelike particles, *Phys. Rev. E* 85 (2012) 011403.
- 473 [19] Z. Luo, H. Song, X. Feng, M. Run, H. Cui, L. Wu, J. Gao, Z. Wang, Liquid crystalline phase  
474 behavior and sol–gel transition in aqueous halloysite nanotube dispersions, *Langmuir* 29  
475 (2013) 12358–12366.
- 476 [20] P. Woolston, J.S. van Duijneveldt, Isotropic-nematic phase transition in aqueous sepiolite  
477 suspensions, *J. Colloid Interface Sci.* 437 (2015) 65–70.  
478 <https://doi.org/10.1016/j.jcis.2014.09.014>.
- 479 [21] S. Manzetti, J.-C.P. Gabriel, Methods for dispersing carbon nanotubes for  
480 nanotechnology applications: liquid nanocrystals, suspensions, polyelectrolytes, colloids and  
481 organization control, *Int. Nano Lett.* 9 (2019) 31–49.
- 482 [22] W. Song, I.A. Kinloch, A.H. Windle, Nematic liquid crystallinity of multiwall carbon  
483 nanotubes, *Science* 302 (2003) 1363–1363.
- 484 [23] S. Badaire, C. Zakri, M. Maugey, A. Derré, J.N. Barisci, G. Wallace, P. Poulin, Liquid  
485 crystals of DNA-stabilized carbon nanotubes, *Adv. Mater.* 17 (2005) 1673–1676.
- 486 [24] V.A. Davis, A.N.G. Parra-Vasquez, M.J. Green, P.K. Rai, N. Behabtu, V. Prieto, R.D. Booker,  
487 J. Schmidt, E. Kesselman, W. Zhou, True solutions of single-walled carbon nanotubes for  
488 assembly into macroscopic materials, *Nat. Nanotechnol.* 4 (2009) 830.
- 489 [25] F. Mirri, R. Ashkar, V. Jamali, L. Liberman, R.A. Pinnick, P. Van Der Schoot, Y. Talmon, P.D.  
490 Butler, M. Pasquali, Quantification of carbon nanotube liquid crystal morphology via  
491 neutron scattering, *Macromolecules* 51 (2018) 6892–6900.
- 492 [26] C.J. Simonsen Ginestra, C. Martínez-Jiménez, A. Matatyaho Ya’akobi, O.S. Dewey, A.D.  
493 Smith McWilliams, R.J. Headrick, J.A. Acapulco, L.R. Scammell, M.W. Smith, D.V. Kosynkin,

494 Liquid crystals of neat boron nitride nanotubes and their assembly into ordered macroscopic  
495 materials, *Nat. Commun.* 13 (2022) 3136.

496 [27] M.R. Ayatollahi, S. Shadlou, M.M. Shokrieh, M. Chitsazzadeh, Effect of multi-walled  
497 carbon nanotube aspect ratio on mechanical and electrical properties of epoxy-based  
498 nanocomposites, *Polym. Test.* 30 (2011) 548–556.

499 [28] J. Guo, Y. Liu, R. Prada-Silvy, Y. Tan, S. Azad, B. Krause, P. Pötschke, B.P. Grady, Aspect  
500 ratio effects of multi-walled carbon nanotubes on electrical, mechanical, and thermal  
501 properties of polycarbonate/MWCNT composites, *J. Polym. Sci. Part B Polym. Phys.* 52  
502 (2014) 73–83.

503 [29] C. Ding, J. Du, Y. Cao, C. Yue, B. Cheng, Effects of the aspect ratio of multi-walled carbon  
504 nanotubes on the structure and properties of regenerated collagen fibers, *Int. J. Biol.*  
505 *Macromol.* 126 (2019) 595–602.

506 [30] E. Paineau, G. Monet, V. Peyre, C. Goldmann, S. Rouzière, P. Launois, Colloidal Stability  
507 of Imogolite Nanotube Dispersions: A Phase Diagram Study, *Langmuir* 35 (2019) 12451–  
508 12459.

509 [31] K. Kajiwara, N. Donkai, Y. Hiragi, H. Inagaki, Lyotropic mesophase of imogolite, 1. Effect of  
510 polydispersity on phase-diagram, *Makromol. Chem.-Macromol. Chem. Phys.* 187 (1986)  
511 2883–2893.

512 [32] N. Donkai, K. Kajiwara, M. Schmidt, T. Miyamoto, Lyotropic mesophase of imogolite -  
513 molecular-weight fractionation and polydispersity effect, *Makromol. Chem.-Rapid Commun.*  
514 14 (1993) 611–617.

515 [33] P. Levitz, M. Zinsmeister, P. Davidson, D. Constantin, O. Poncelet, Intermittent Brownian  
516 dynamics over a rigid strand: Heavily tailed relocation statistics in a simple geometry, *Phys.*  
517 *Rev. E* 78 (2008) 030102. <https://doi.org/10.1103/PhysRevE.78.030102>.

518 [34] E. Paineau, M.-E.M. Krapf, M.-S. Amara, N.V. Matskova, I. Dozov, S. Rouzière, A. Thill, P.  
519 Launois, P. Davidson, A liquid-crystalline hexagonal columnar phase in highly-dilute  
520 suspensions of imogolite nanotubes, *Nat. Commun.* 7 (2016) 10271.  
521 <https://doi.org/10.1038/ncomms10271>.

522 [35] C.-Y. Su, Q. Lyu, D.-Y. Kang, Z.-H. Yang, C.H. Lam, Y.-H. Chen, S.-C. Lo, C.-C. Hua, L.-C. Lin,  
523 Hexagonal Superalignment of Nano-Objects with Tunable Separation in a Dilute and Spacer-  
524 Free Solution, *Phys. Rev. Lett.* 123 (2019) 238002.

525 [36] J. Harsh, S. Traina, J. Boyle, Y. Yang, Adsorption of cations on imogolite and their effect  
526 on surface-charge characteristics, *Clays Clay Miner.* 40 (1992) 700–706.

527 [37] J.P. Gustafsson, The surface chemistry of imogolite, *Clays Clay Miner.* 49 (2001) 73–80.

528 [38] N. Arancibia-Miranda, M. Escudey, M. Molina, M. Teresa Garcia-Gonzalez, Use of  
529 isoelectric point and pH to evaluate the synthesis of a nanotubular aluminosilicate, *J. Non-*  
530 *Cryst. Solids* 357 (2011) 1750–1756.

531 [39] C. Hamon, E. Beaudoin, P. Launois, E. Paineau, Doping liquid crystals of colloidal  
532 inorganic nanotubes by additive-free metal nanoparticles, *J. Phys. Chem. Lett.* 12 (2021)  
533 5052–5058.

534 [40] E. Paineau, S. Rouzière, G. Monet, C.C. Diogo, I. Morfin, P. Launois, Role of initial  
535 precursors on the liquid-crystalline phase behavior of synthetic aluminogermanate  
536 imogolite nanotubes, *J. Colloid Interface Sci.* 580 (2020) 275–285.  
537 <https://doi.org/10.1016/j.jcis.2020.07.036>.

- 538 [41] E. Paineau, P. Launois, Influence of the Al/Ge Ratio on the Structure and Self-  
539 Organization of Anisometric Imogolite Nanotubes, *Crystals* 10 (2020) 1094.
- 540 [42] T. Cao, M. Elimelech, Colloidal stability of cellulose nanocrystals in aqueous solutions  
541 containing monovalent, divalent, and trivalent inorganic salts, *J. Colloid Interface Sci.* 584  
542 (2021) 456–463.
- 543 [43] C. Browne, V.S. Raghuwanshi, G. Garnier, W. Batchelor, Modulating the chiral nematic  
544 structure of cellulose nanocrystal suspensions with electrolytes, *J. Colloid Interface Sci.* 650  
545 (2023) 1064–1072.
- 546 [44] W.J. Lee, E. Paineau, D.B. Anthony, Y. Gao, H.S. Leese, S. Rouzière, P. Launois, M.S.P.  
547 Shaffer, Inorganic Nanotube Mesophases Enable Strong Self-Healing Fibers, *ACS Nano* 14  
548 (2020) 5570–5580.
- 549 [45] C. Takeshita, K. Masuda, M. Kobayashi, The effect of monovalent anion species on the  
550 aggregation and charging of allophane clay nanoparticles, *Colloids Surf. Physicochem. Eng.*  
551 *Asp.* 577 (2019) 103–109.
- 552 [46] M. Li, M. Kobayashi, The aggregation and charging of natural clay allophane: Critical  
553 coagulation ionic strength in the presence of multivalent counter-ions, *Colloids Surf.*  
554 *Physicochem. Eng. Asp.* 626 (2021) 127021.
- 555 [47] M. Li, T. Sugimoto, Y. Yamashita, M. Kobayashi, Aggregation and charging of natural  
556 allophane particles in the presence of oxyanions, *Colloids Surf. Physicochem. Eng. Asp.* 649  
557 (2022) 129413.
- 558 [48] G. Trefalt, I. Szilagyi, G. Tellez, M. Borkovec, Colloidal stability in asymmetric electrolytes:  
559 Modifications of the Schulze–Hardy rule, *Langmuir* 33 (2017) 1695–1704.
- 560 [49] J.F. Moore, E. Paineau, P. Launois, M.S. Shaffer, Continuous Binder-Free Fibers of Pure  
561 Imogolite Nanotubes, *ACS Appl. Mater. Interfaces* 13 (2021) 17940–17947.
- 562 [50] M.-S. Amara, E. Paineau, M. Bacia-Verloop, M.-E.M. Krapf, P. Davidson, L. Belloni, C.  
563 Levard, J. Rose, P. Launois, A. Thill, Single-step formation of micron long (OH)3Al2O3Ge(OH)  
564 imogolite-like nanotubes, *Chem. Commun.* 49 (2013) 11284–11286.
- 565 [51] E. Paineau, M.S. Amara, G. Monet, V. Peyre, S. Rouzière, P. Launois, Effect of Ionic  
566 Strength on the Bundling of Metal Oxide Imogolite Nanotubes, *J. Phys. Chem. C* 121 (2017)  
567 21740–21749.
- 568 [52] J. Schindelin, I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S. Preibisch,  
569 C. Rueden, S. Saalfeld, B. Schmid, Fiji: an open-source platform for biological-image analysis,  
570 *Nat. Methods* 9 (2012) 676.
- 571 [53] F. Camerel, J.-C.P. Gabriel, P. Batail, P. Davidson, B. Lemaire, M. Schmutz, T. Gulik-  
572 Krzywicki, C. Bourgaux, Original Single Walled Nanotubules Based on Weakly Interacting  
573 Covalent Mineral Polymers,  $1\infty$ [Nb2PS10-] in N-Methylformamide, *Nano Lett.* 2 (2002) 403–  
574 407.
- 575 [54] A. Guinier, G. Fournet, K.L. Yudowitch, Small-angle scattering of X-rays, (1955).
- 576 [55] E.E. Maier, R. Krause, M. Deggelmann, M. Hagenbuechle, R. Weber, S. Fraden, Liquidlike  
577 order of charged rodlike particle solutions, *Macromolecules* 25 (1992) 1125–1133.
- 578 [56] C. Baravian, L.J. Michot, E. Paineau, I. Bihannic, P. Davidson, M. Imperor-Clerc, E.  
579 Belamie, P. Levitz, An effective geometrical approach to the structure of colloidal  
580 suspensions of very anisometric particles, *Epl* 90 (2010) 36005.  
581 <https://doi.org/10.1209/0295-5075/90/36005>.

- 582 [57] P.A. Buining, A.P. Philipse, H.N.W. Lekkerkerker, Phase behavior of aqueous dispersions  
583 of colloidal boehmite rods, *Langmuir* 10 (1994) 2106–2114.
- 584 [58] G. Lagaly, I. Dékány, *Colloid clay science*, in: *Dev. Clay Sci.*, Elsevier, 2013: pp. 243–345.
- 585 [59] M.J. Vold, Sediment volume and structure in dispersions of anisometric particles, *J. Phys.*  
586 *Chem.* 63 (1959) 1608–1612.
- 587 [60] T. Narayanan, H. Wacklin, O. Konovalov, R. Lund, Recent applications of synchrotron  
588 radiation and neutrons in the study of soft matter, *Crystallogr. Rev.* 23 (2017) 160–226.
- 589 [61] M. Gvaramia, G. Mangiapia, V. Pipich, M.-S. Appavou, S. Jaksch, O. Holderer, M.D.  
590 Rukhadze, H. Frielinghaus, Tunable viscosity modification with diluted particles: when  
591 particles decrease the viscosity of complex fluids, *Colloid Polym. Sci.* 297 (2019) 1507–1517.
- 592 [62] A.K. Tripathi, Ionic liquid–based solid electrolytes (ionogels) for application in  
593 rechargeable lithium battery, *Mater. Today Energy* 20 (2021) 100643.
- 594 [63] N. Kapernaum, A. Lange, M. Ebert, M.A. Grunwald, C. Haege, S. Marino, A. Zens, A.  
595 Taubert, F. Giesselmann, S. Laschat, Current topics in ionic liquid crystals, *ChemPlusChem* 87  
596 (2022) e202100397.
- 597 [64] Y. Zhao, G. Cavallaro, Y. Lvov, Orientation of charged clay nanotubes in evaporating  
598 droplet meniscus, *J. Colloid Interface Sci.* 440 (2015) 68–77.
- 599 [65] C. Bruel, T.S. Davies, P.J. Carreau, J.R. Tavares, M.-C. Heuzey, Self-assembly behaviors of  
600 colloidal cellulose nanocrystals: A tale of stabilization mechanisms, *J. Colloid Interface Sci.*  
601 574 (2020) 399–409.
- 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  $\phi$  and electrolytes ( $IS = 10^{-3}$   
611  $\text{mol.L}^{-1}$ ). (a,d) NaCl; (b,e)  $\text{Na}_2\text{SO}_4$ ; (c,f)  $\text{Na}_3\text{PO}_4$ . 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  $\phi$  with NaCl ( $IS = 10^{-3} \text{ mol.L}^{-1}$ ). The images on the right are taken with  
617 the addition of a retardation filter ( $\lambda$ -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)  $\text{Na}_2\text{SO}_4$ ; (c,f)  $\text{Na}_3\text{PO}_4$ .

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,  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_3\text{PO}_4$ ) 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<sub>5d</sub>  
628 (*left*) and DW<sub>20d</sub> (*right*) dispersions at various volume fractions  $\phi$  with (a,b) NaCl; (c,d) Na<sub>2</sub>SO<sub>4</sub>  
629 and (e,f) Na<sub>3</sub>PO<sub>4</sub> 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  $\phi$ . 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<sup>-1</sup>, 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  $\phi$  for DW<sub>5d</sub> and DW<sub>20d</sub>  
642 with NaCl, Na<sub>2</sub>SO<sub>4</sub> and Na<sub>3</sub>PO<sub>4</sub> 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<sup>a,\*</sup>, Léna LE ROUX<sup>a</sup>, Claire GOLDMANN<sup>a</sup>, Stéphan ROUZIÈRE<sup>a</sup>,

650 Pascale LAUNOIS<sup>a</sup>, Thomas BIZIEN<sup>b</sup>, Erwan PAINEAU<sup>a,\*</sup>

651

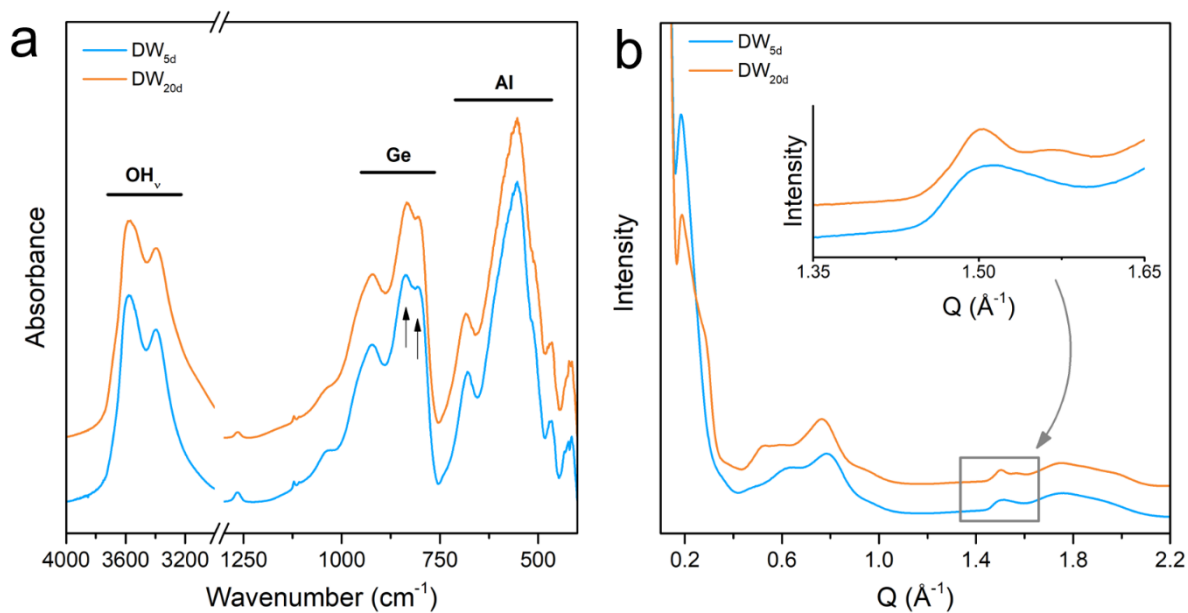
652

## 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  $\text{cm}^{-1}$ . The obtained spectra (Figure S1a) display the vibrations of imogolite nanotubes at  
660  $910 \text{ cm}^{-1}$  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  $\text{GeO}_4$  structures, while the absorption bands at 690, 555 and 420  
663  $\text{cm}^{-1}$  are related to Al-O vibrations in the INT structure.<sup>S1,S2</sup> In addition, FTIR curves  
664 present two broad peaks at  $3580$  and  $3400 \text{ cm}^{-1}$  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 (WJMGlas/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.<sup>S3</sup> In particular, the enhanced intensity between  $0.4$  and  
677  $0.9 \text{ \AA}^{-1}$  is characteristic of the mean inter-wall distance in a double-walled nanotube.<sup>S4,S5</sup>  
678 The 002 asymmetric peak around  $1.5 \text{ \AA}^{-1}$  is a signature of the one-dimensional  
679 periodicity along the nanotube axis,<sup>S6</sup> the period being equal to  $\sim 8.5 \text{ \AA}$ .

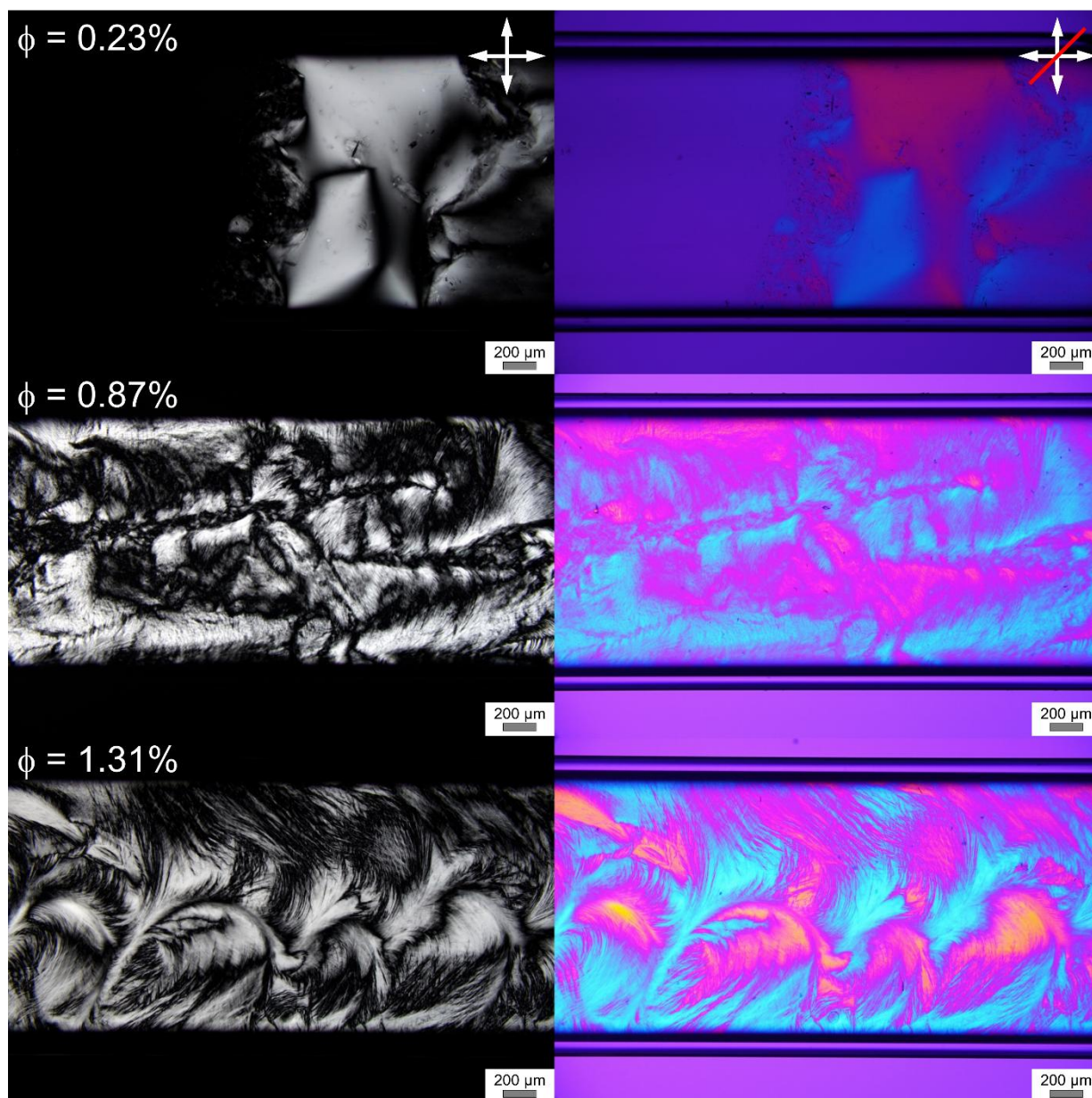
680



681  
 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<sup>-1</sup> 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.

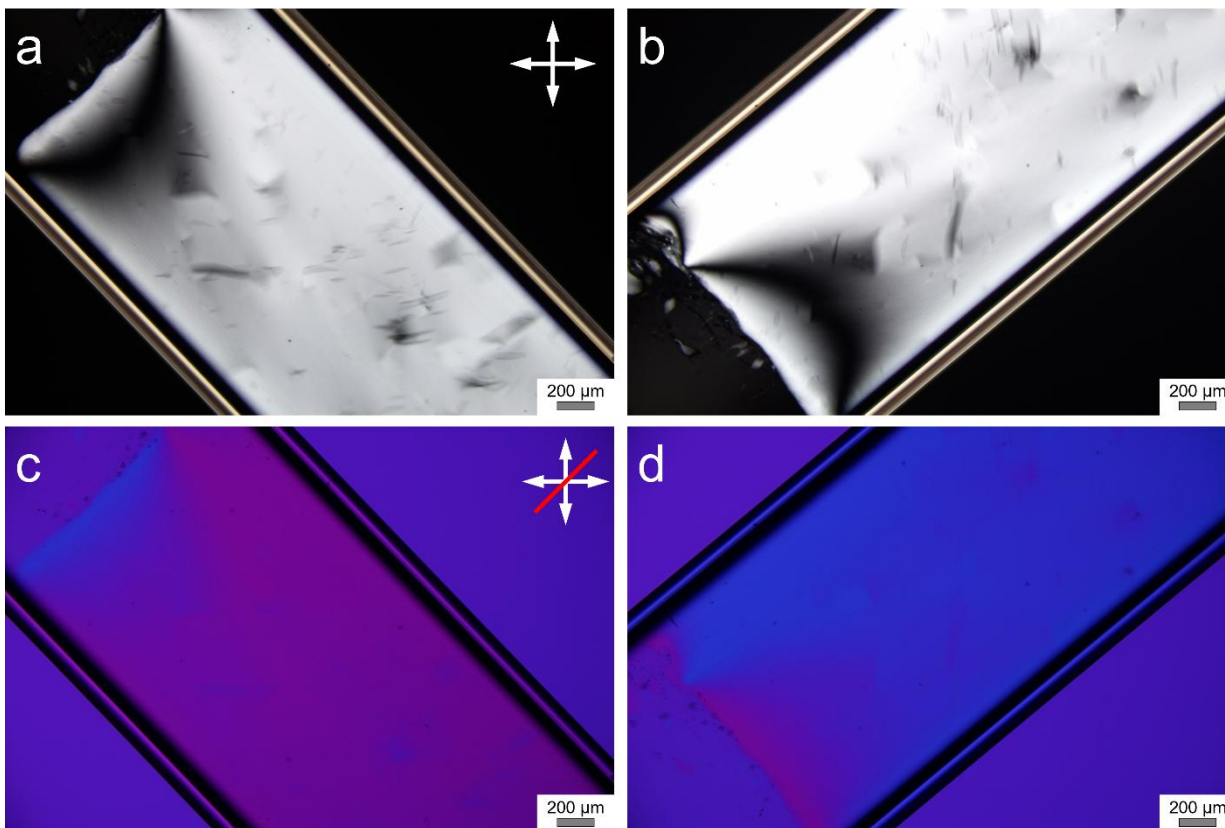
687  
688

## 2. Polarized optical microscopy



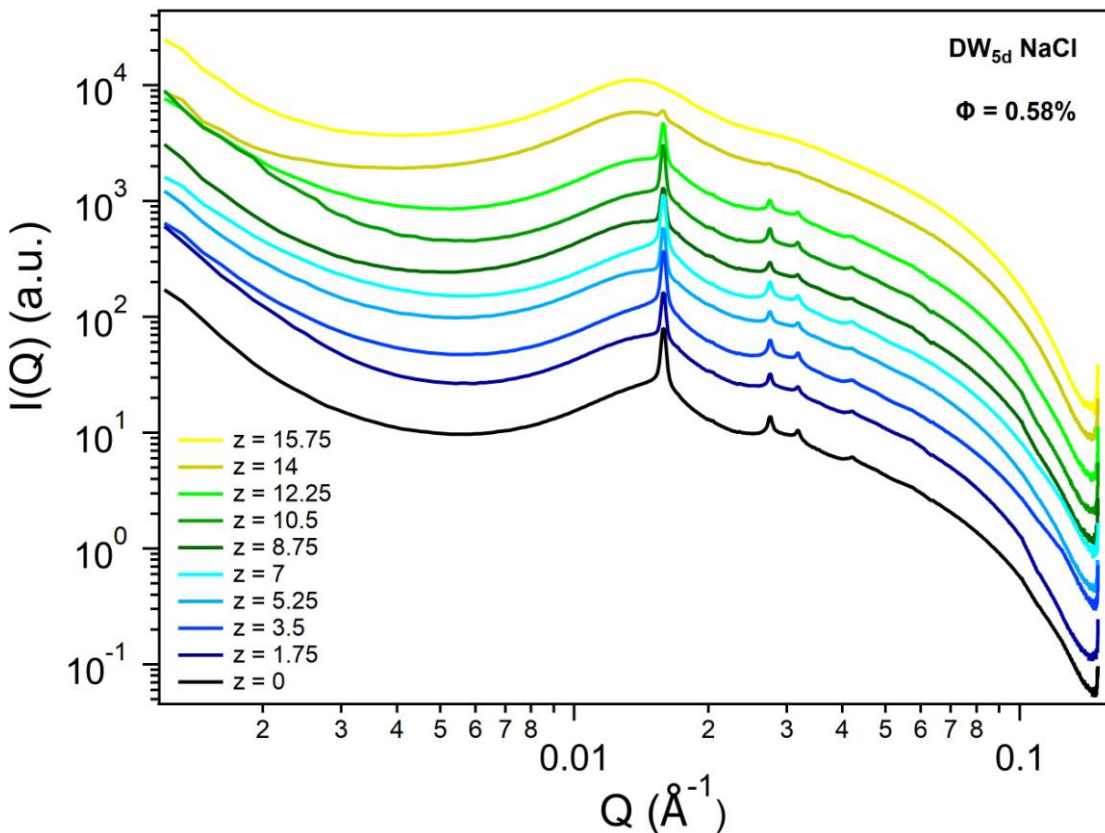
689

690 **Fig. S2.** Polarized optical microscopy observations of  $DW_{5d}$  aqueous dispersions  
691 prepared at different volume fractions  $\phi$  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 ( $\lambda$ -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.  
695



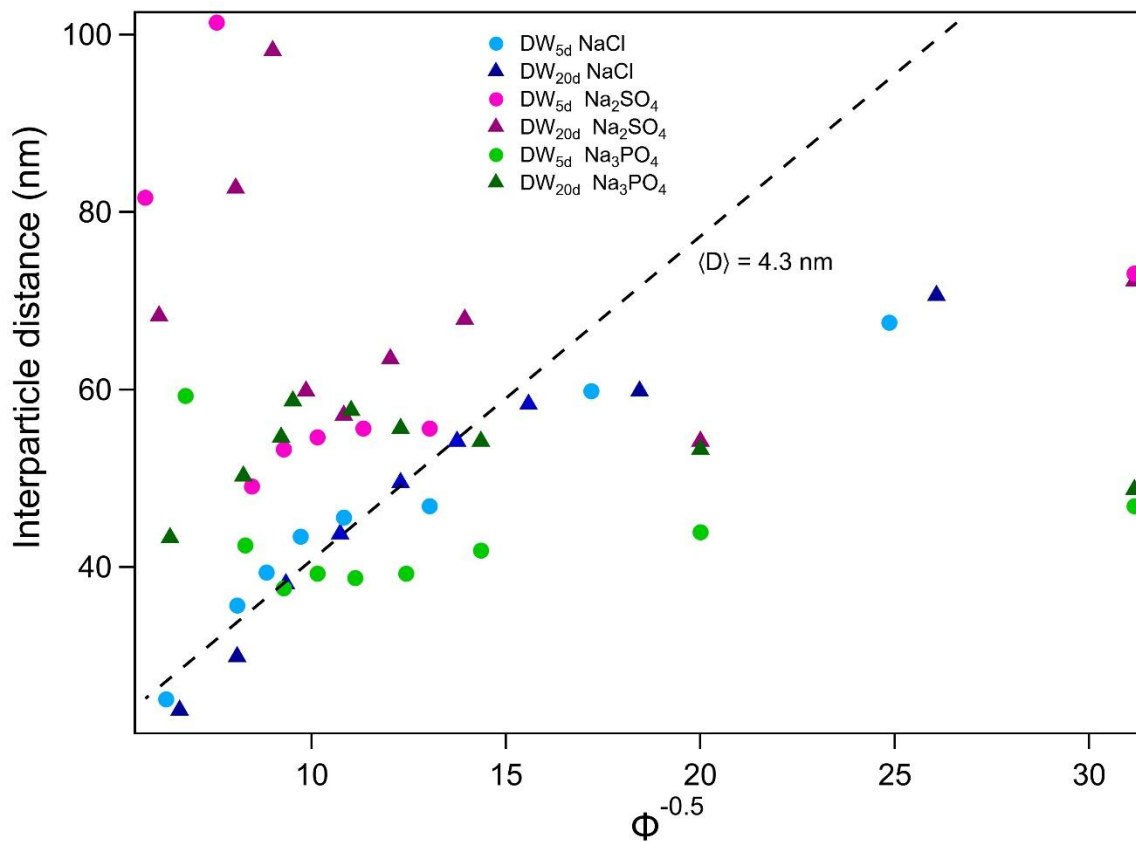
696  
 697  
 698 **Fig. S3.** Optical textures in polarized light microscopy of DW<sub>20d</sub> aqueous dispersions ( $\phi$   
 699 = 0.1%,  $[\text{NaCl}] = 10^{-3} \text{ mol.L}^{-1}$ ) without (a,b) and with (c,d) a retardation filter ( $\lambda$ -plate, 530  
 700 nm). The sample is tilted by 45° clockwise (a,c) and counter-clockwise (b,d). The white  
 701 arrows and the red line indicate the orientation of the polarizers and the slow axis of the  
 702 retardation filter, respectively.  
 703  
 704

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



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

715 **4. Swelling laws**  
 716



717  
 718 **Fig. S5.** Evolution of the interparticle distance with  $\phi^{-0.5}$  for aqueous dispersions of DW<sub>5d</sub>  
 719 (circles) and DW<sub>20d</sub> (triangles) as a function of the electrolytes ( $IS = 10^{-3}$  mol.L<sup>-1</sup>). 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<sup>S7</sup>:

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

with  $n$  the number density of ions in the suspension,  $e$  the proton charge and  $\psi_0$  the particle surface potential. We take  $\psi_0 = 50$  mV deduced from previous zeta-potential measurements on DWINTs.<sup>S2</sup>  $\kappa$  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<sup>-1</sup>). 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),<sup>S8</sup> 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**

- 751
- 752 [S1] S. Wada, K. Wada, Effects of substitution of germanium for silicon in imogolite,  
753 *Clays Clay Miner.* 30 (1982) 123–128.
- 754 [S2] E. Paineau, S. Rouzière, G. Monet, C.C. Diogo, I. Morfin, P. Launois, Role of  
755 initial precursors on the liquid-crystalline phase behavior of synthetic  
756 aluminogermanate imogolite nanotubes, *J. Colloid Interface Sci.* 580 (2020) 275–  
757 285.
- 758 [S3] E. Paineau, G. Monet, V. Peyre, C. Goldmann, S. Rouzière, P. Launois, Colloidal  
759 Stability of Imogolite Nanotube Dispersions: A Phase Diagram Study, *Langmuir* 35  
760 (2019) 12451–12459.
- 761 [S4] J. Cambedouzou, M. Chorro, R. Almairac, L. Noé, E. Flahaut, S. Rols, M.  
762 Monthieux, P. Launois, X-ray diffraction as a tool for the determination of the  
763 structure of double-walled carbon nanotube batches, *Phys. Rev. B* 79 (2009)  
764 195423.
- 765 [S5] P. Maillet, C. Levard, E. Larquet, C. Mariet, O. Spalla, N. Menguy, A. Masion, E.  
766 Doelsch, J. Rose, A. Thill, Evidence of Double-Walled Al-Ge Imogolite-Like  
767 Nanotubes. A Cryo-TEM and SAXS Investigation, *J. Am. Chem. Soc.* 132 (2010)  
768 1208–1209.
- 769 [S6] G. Monet, M.S. Amara, S. Rouzière, E. Paineau, Z. Chai, J.D. Elliott, E. Poli, L.-  
770 M. Liu, G. Teobaldi, P. Launois, Structural resolution of inorganic nanotubes with  
771 complex stoichiometry, *Nat. Commun.* 9 (2018) 2033.
- 772 [S7] P.A. Buining, A.P. Philipse, H.N.W. Lekkerkerker, Phase behavior of aqueous  
773 dispersions of colloidal boehmite rods, *Langmuir* 10 (1994) 2106–2114.
- 774 [S8] R.G. Horn, D.R. Clarke, M.T. Clarkson, Direct measurement of surface forces  
775 between sapphire crystals in aqueous solutions, *J. Mater. Res.* 3 (1988) 413–416.  
776