

## Supporting information

### Chemical affinity and dispersibility of boron nitride nanotubes

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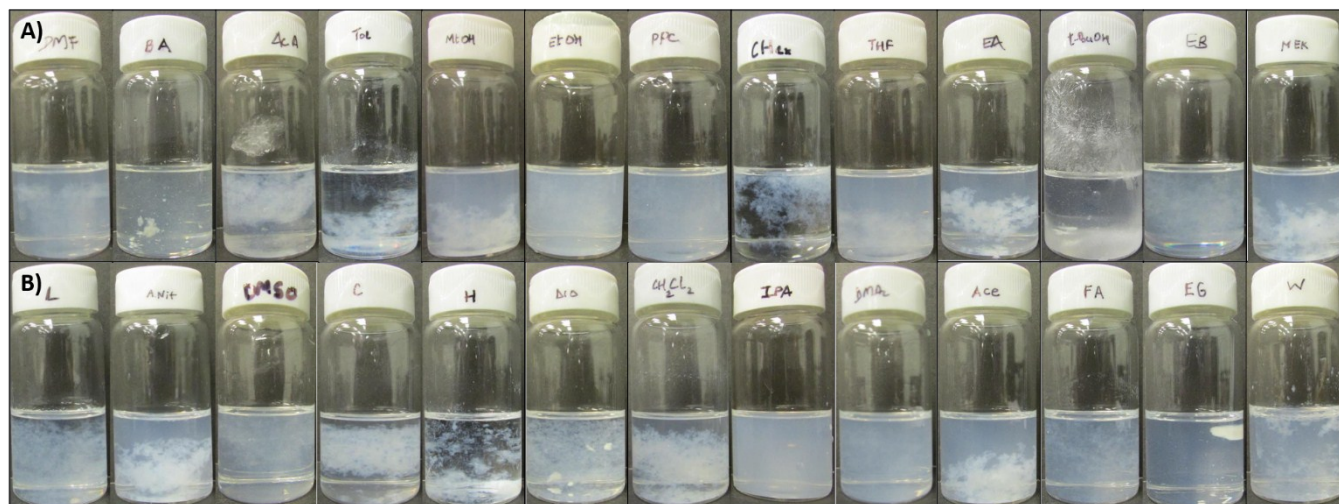
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This supporting information gathers the purity, supplier and physical properties (density, viscosity and molar volume) of the solvents that were employed for the dispersions. It also includes the pictures of the vials taken immediately after sonication, after 150 h of settling and after their sedimentation time. Finally, it includes the mathematical analysis for the calculation of HSP using the *HSPiP* software.

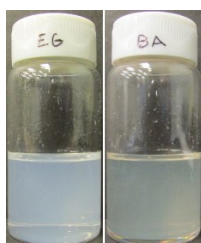
**Table S1** Purity, supplier and physical properties of the solvents used in the sedimentation tests.

| Solvent                | Purity (%)    | Supplier            | Density <sup>a</sup> at 20°C (g/cm <sup>3</sup> ) | Viscosity <sup>a</sup> at 20°C (mPa s) | Molar volume (cm <sup>3</sup> /mol) | Ref       |
|------------------------|---------------|---------------------|---|--|-------------------------------------|-----------|
| N,N'-Dimethylacetamide | 99.5          | Anachemia           | 0.937 (25)  | 0.945 (25)                             | 92.5                                | 1-3       |
| N,N'-Dimethylformamide | 99.8          | Sigma-Aldrich       | 0.95  | 0.82                                   | 77.0                                | 3,4       |
| Acetone                | ≥ 99.5        | Fisher Chemical     | 0.79  | 0.35                                   | 74.0                                | 3,4       |
| Methanol               | 99.9          | Fisher Chemical     | 0.79  | 0.59                                   | 40.7                                | 3,4       |
| 2-Propanol             | 99            | Laboratoire MAT     | 0.786   | 1.96 (25)                              | 76.8                                | 3,5,6     |
| Tetrahydrofuran        | ≥ 99.9        | Sigma-Aldrich       | 0.89  | 0.55                                   | 81.7                                | 3,4       |
| Chloroform             | 99.9          | Fisher Scientific   | 1.48  | 0.37                                   | 80.7                                | 3,4       |
| Acetic acid            | ≥ 99.7        | Laboratoire MAT     | 1.049   | 1.037 (30)                             | 57.1                                | 7,8       |
| Dimethylsulfoxide      | > 99.9        | Alfa Aesar          | 1.1   | 1.98                                   | 71.3                                | 3,4       |
| Toluene                | 99.9          | Fisher Chemical     | 0.87  | 0.59                                   | 106.8                               | 3,4       |
| Cyclohexane            | 99.9          | Fisher Chemical     | 0.78  | 1                                      | 108.7                               | 3,4       |
| Heptane                | Not specified | Fisher Chemical     | 0.679   | 0.393                                  | 147.4                               | 3,4,9     |
| Ethyl acetate          | 99.9          | Fisher Chemical     | 0.89  | 0.44                                   | 98.5                                | 3,4       |
| d-Limonene             | 96            | Acros Organics      | 0.841   | 0.897                                  | 162.9                               | 3,4,9     |
| Formamide              | 99            | Alfa Aesar          | 1.13  | 3.3                                    | 39.9                                | 3,4       |
| 1,4-Dioxane            | > 99          | Alfa Aesar          | 1.04  | 1.31                                   | 85.7                                | 3,4       |
| Acetonitrile           | ≥ 99.5        | Laboratoire MAT     | 0.786(25)   | 0.35                                   | 52.9                                | 3,4,10,11 |
| Ethylenglycol          | ≥ 99.8        | Fisher scientific   | 1.12  | 20.9                                   | 55.9                                | 3,4       |
| Ethanol                | 95            | Commercial alcohols | 0.82  | 1.22                                   | 58.6                                | 3,4       |
| Propylene carbonate    | 99.5          | Acros Organics      | 1.2   | 2.8                                    | 85.2                                | 3,4       |
| Benzyl alcohol         | >99           | Sigma-Aldrich       | 1.0419 (24)                                       | 5.474 (25)                             | 103.8                               | 3,4,12    |
| Ethyl benzoate         | 99            | Alfa Aesar          | 1.04  | 1.83                                   | 144.1                               | 3,4,9     |
| tert-Butanol           | ≥99           | Sigma-Aldrich       | 0.81 (25)   | 3.35                                   | 95.8                                | 3,4,13,14 |
| Dichloromethane        | 99            | Alfa Aesar          | 1.33  | 0.43                                   | 64.4                                | 3,4       |
| Methyl ethyl ketone    | ≥99           | Sigma-Aldrich       | 0.8   | 0.386                                  | 90.2                                | 3,4,9     |
| Water                  | DI            | -                   | 0.997   | 0.89                                   | 18                                  | 3,4,9     |

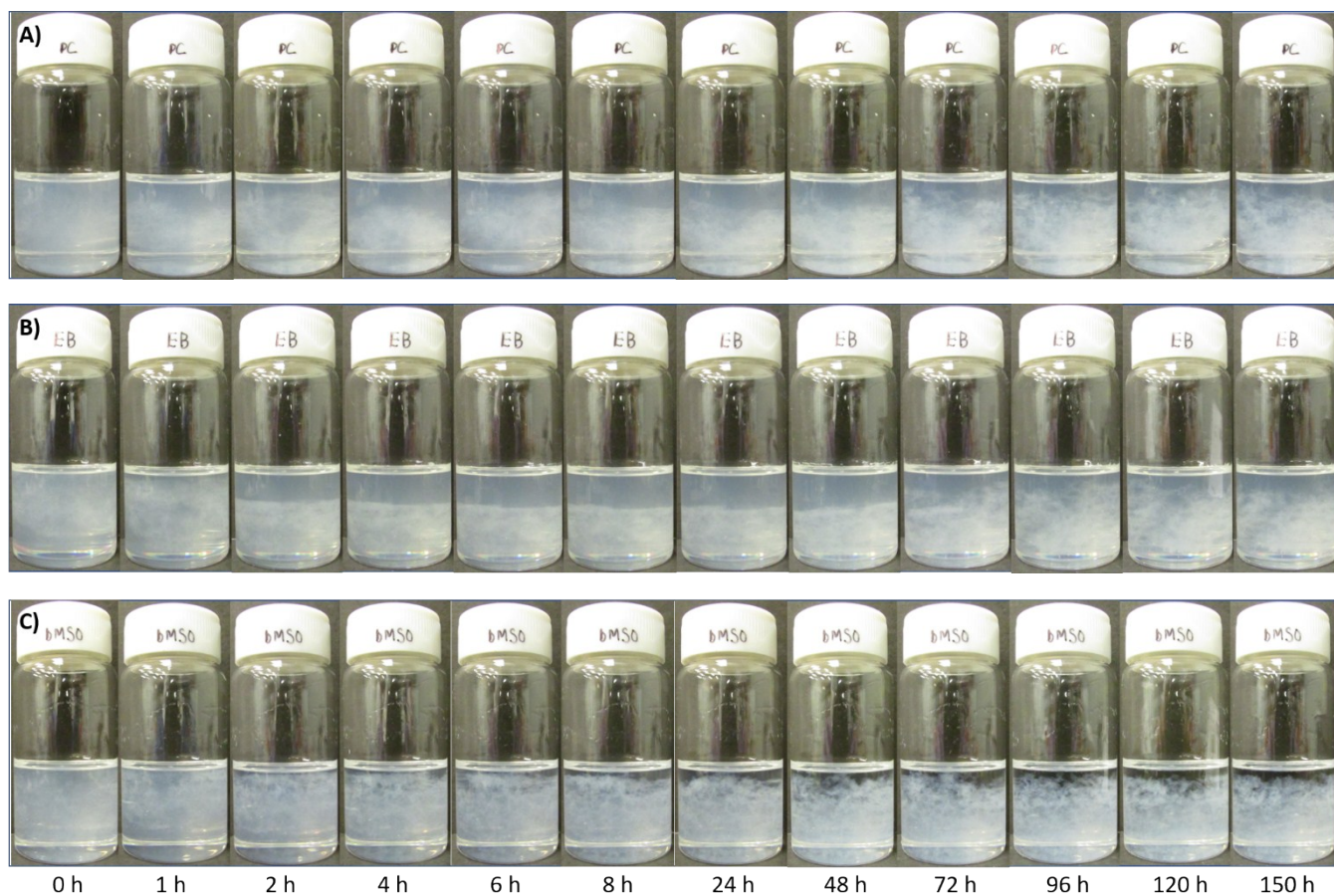
<sup>a</sup> When different from 20°C, the temperature is specified in parenthesis in °C.



**Figure S1** Pictures of the dispersions taken immediately after sonication. Solvents from left to right are: **(A)** DMF, benzyl alcohol, acetic acid, toluene, methanol, ethanol, propylene carbonate, cyclohexane, THF, ethyl acetate, tert-butanol, ethyl benzoate and **(B)** MEK, d-limonene, acetonitrile, DMSO, chloroform, heptane, 1,2-dioxane, dichloromethane, 2-propanol, DMAc, acetone, formamide, ethylene glycol and water.

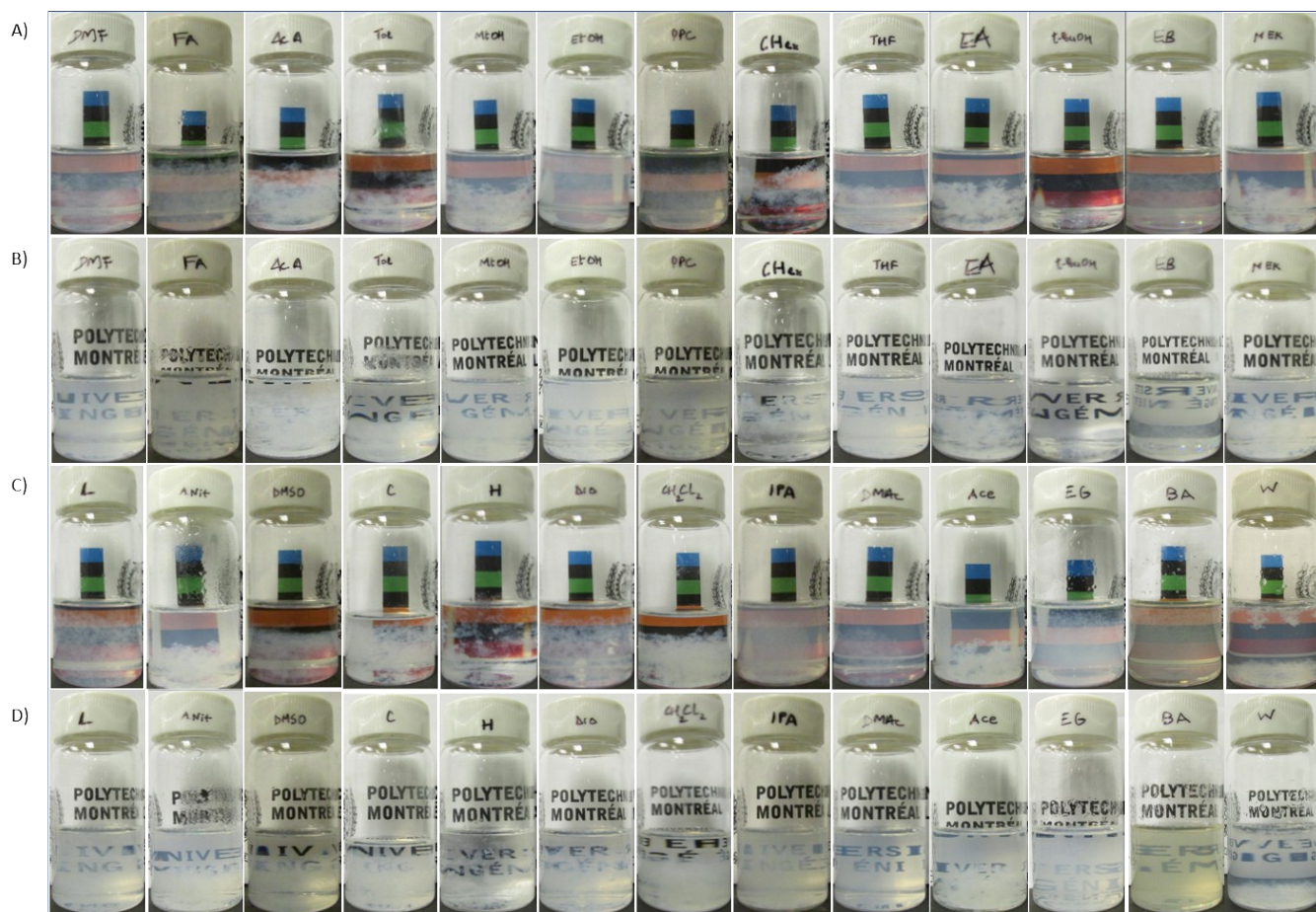


**Figure S2** BNNTs dispersions in ethylene glycol and benzyl alcohol applying high energy during sonication.



**Figure S3** Evolution of the dispersion state over time in A) propylene carbonate, B) ethyl benzoate and C) DMSO. Pictures of the vials were taken at 0, 1, 2, 4, 6, 8, 24, 48, 72, 96, 120 and 150 h after sonication.





**Figure S4** Pictures of the vials taken after a relative sedimentation time (RST) of  $1.0295 \times 10^{11} \text{ s}^2/\text{m}^2$ . Solvents from left to right are: **(A,B)** *N,N'*-dimethylformamide, formamide, acetic acid, toluene, methanol, ethanol, propylene carbonate, cyclohexane, tetrahydrofuran, ethyl acetate, tert-butanol, ethyl benzoate, methyl ethyl ketone and **(C,D)** d-limonene, acetonitrile, dimethyl sulfoxide, chloroform, heptane, 1,4-dioxane, dichloromethane, 2-propanol, *N,N'*-dimethylacetamide, acetone, ethylene glycol, benzyl alcohol and water.

## Mathematical analysis

Classification of the dispersions in good (score = 1) and bad ones (score = 0) must be done prior the mathematical analysis. Then, “0” or “1” is inputted into the *HSPiP* software. Calculations are performed based on the *desirability function* FIT (eq. S1)<sup>4</sup>

$$FIT = (A_1 * A_2 * \dots A_n)^{1/n} \quad (S1)$$

where  $n$  refers to the number of solvents considered in the experiment. FIT tends towards 1 when most of good solvents fit inside a sphere and most of bad solvents are excluded. The coefficient  $A_i$  can be calculated according to the equations presented in table S2. This coefficient will be equal to 1 when a given good solvent is inside the sphere or when a poor one is outside. The error distance refers to the separation between the solvent in error and the border of the sphere. A solvent in error happen when a good solvent is outside the sphere or when a bad solvent is inside. These errors may be attributed to low molecular volumes of the solvents.<sup>4</sup>

Table S2. Equation to calculate coefficient  $A_i$ .

|              | RED $\leq$ 1.0           | RED $>$ 1.0              |
|--------------|--------------------------|--------------------------|
| Good solvent | $A_i = 1$                | $A_i = e^{+(R_o - R_a)}$ |
| Poor solvent | $A_i = e^{+(R_a - R_o)}$ | $A_i = 1$                |

Taking as a starting point the average of Hansen parameters for the good solvents, the calculations are started. Then, the *SPHERE* program determines eight points, corresponding to the corners of a cube, which center is defined by the current best values. During the calculations, different radii are tested at every corner of the cube. While improving the fit, a new center of the cube is determined. This process continues until the FIT can not longer be improved.<sup>4</sup>

While doing HSP experiments, two types of errors may occur. The first one, known as systematic error, is related to the molar volume of the species involved. The molecular size of solvent and solute considerably impacts the solubility, but also other processes such as diffusion, permeation or resistance to chemicals. Molecules with smaller sizes will tend to solubilize more than molecules with larger sizes. This is supported by Hildebrand solubility theory, where it is stated that solvents with low molar volumes are preferred over those with larger ones, despite their similarity in solubility parameters. The Flory-Huggins theory also points out that better solubility is expected when using small molecules of solvent.<sup>4</sup>

Beyond solute size and shape, kinetic phenomena should be considered. Diffusion occurs faster when linear and small molecules are used. In fact, it could happen that equilibrium is not reached when large and bulky molecules are used, due to a low diffusion coefficient. This situation has been observed for example, when thick rigid polymers are dispersed in organic solvents.<sup>4</sup>

Due to the reasons mentioned above, it was thought that an extra solubility parameter based on the solvent molecular volume was needed. This was studied in some works, but it was concluded that size effects are mainly caused by kinetic phenomena and not by thermodynamic principles, on which solubility theory is based. However, there is a strong relationship between the segment size parameter ( $\rho$ ) from the Prigogine theory and the dispersibility parameter ( $\delta_d$ ) from the Hansen solubility approach. This may lead to the conclusion that molecular size has an influence on the dispersibility parameter. For example, when  $\delta_d$  is calculated for aliphatic hydrocarbons, molecules with larger molecular size such as aromatic rings possess higher  $\delta_d$ . Thus, when analyzing the results obtained by HSPiP, it may happen that solvent molecular size is a significant parameter for the prediction of HSP of the solute in question.<sup>4</sup>

The second type of error encountered when doing the HSPiP runs may be due to not expected interactions, such as reactions between solvent and solute. A common practice to minimize the errors is to analyze the output data marked with “\*”. When doing the calculations, the aim of the SPHERE program is to minimize the radius of the sphere while having the maximum DATA FIT (1.0).<sup>4</sup>

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