Electronic Supplementary Material

Solvent-controlled reversible switching between adsorbed self-assembled nanoribbons and nanotubes

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S-1. FTIR spectra analysis of BHPB-10 behavior in solvents and in dried states

Two solvents, cyclohexane and cyclohexanone, were used in our study to dissolve BHPB-10 molecules. At room temperature, the apolar **cyclohexane** is a poor solvent for BHPB-10, hence the BHPB-10 suspensions need to be heated up to 60° - 65°C for 6-12 h (depending on concentration) to completely dissolve BHPB-10. Then solutions can be diluted with hot solvent and finally cooled down; they gelatinize after few hours at room temperatures (~24 hours are needed for complete gelation and structure formation).

On the contrary, the polar **cyclohexanone** is a good solvent for BHPB-10, which thus can be dissolved in cyclohexanone by periodic shaking of the vial during few hours at room temperature.

FTIR spectra allow us to understand the reasons of such different solubilities of BHPB-10 and allow to follow specific intra- and inter-molecule interactions during BHPB-10 dissolution and drying.

Experimental

FTIR spectra were measured with a Vertex 70 from Bruker.

Solution spectra: The solutions were inserted in a homemade CaF₂ cell, with an optical path of 0.1 mm. The reference spectrum was obtained with an empty cell and the signal of cyclohexanone was not compensated.

Dry sample spectra: We measured also the spectra of BHPB-10 aggregates that were formed from various cyclohexanone solutions after drop-casting on various surfaces.

Spectra of BPBH-10 solutions

FTIR spectra of solutions of BHPB-10 in cyclohexane and in cyclohexanone are shown in Fig.S-1. The **amide A mode** (corresponding to NH stretching) has its maximum located at 3297 cm⁻¹ in cyclohexanone and at 3303 cm⁻¹ in cyclohexane. Both values show the amide hydrogen is H-bonded (free amide hydrogen has maximum at 3450cm⁻¹, cf. spectrum of BHPB-10 in chloroform where the amide hydrogen is not bonded). These bands have a different shape: in cyclohexane the band can be deconvoluted in two peaks, which shows that it arises from different modes and hints that the structure organization is less symmetrical.



Fig. S-1 FTIR spectra of BHPB-10 solutions and respective pure solvents (from top to bottom): BHPB-10/cyclohexanone (10 wt. %);, BHPB-10/cyclohexane/cyclohexanone (10 wt. % in 1:1 mixture); cyclohexanone, BHPB-10/cyclohexane (2 wt. %);, cyclohexane; BHPB-10/CHCl₃ (2 wt. %); CHCl₃. (a) NH stretching region; (b) CO stretching region.

Apparently, the amide inside an H-bond-stabilized supramolecular structure (as in cyclohexane) is less symmetrical than the one in a simple solvated state (as in cyclohexanone where the ketone functional group of the solvent interacts with NH group of the BHPB-10), hence the differences observed in the amide A mode inside these two solvents. Interestingly, already in a 1:1 mixture we observed a strong signature of the 3303 band, that means that the amides start to aggregate into characteric shape of supramolecular structure (as in cyclohexane) despite strong solvation from cyclohexanone. Hence, during the experiment with nanotube dissolution in such 1:1 mixture and then drop-casting (as described in the manuscript) the system can pass from the stage of a weak supramolecular structure (probably, a solution containing short and defective nanotubes surrounded by monomeric BHPB-10) to complete nanotube dissolution (as the cyclohexane is evaporating), then to the formation of 2D symmetric lamellae on the surface (in concentrated solution in cyclohexanone), and then to nanoribbons formation.

Also in the CO stretching area, both spectra are different. The **amide II modes** (combination of C-N stretching and CNH bending) are located at different frequencies 1539 and 1550 cm⁻¹. The amide A and amide II modes clearly show that the NH groups of the amides are involved in H-bonds of different kinds.

The **amide I mode** (mainly due to CO stretching) is located at 1641 cm⁻¹ in cyclohexane. In cyclohexanone, BHPB-10 shows two amide I modes, at 1637 and 1674 cm⁻¹, clearly visible, although close to the absorption band of the solvent. The first one corresponds to H-bonds between BHPB-10. The second corresponds to free carbonyls. It is more intense than the first one. Moreover, the molar extinction coefficient of free carbonyls is much lower than those of the H-bonded ones. One can conclude that in cyclohexanone most of the BHPB-10 carbonyls are free. In cyclohexane, the amides are linked to each other. In cyclohexanone, the NH are linked to the solvent, the CO of BHPB-10 are not bonded.

Around 1600 cm⁻¹, the CC stretching modes of the aromatic rings give rise to peaks with different shifts and shapes, which suggests that the interactions involving the BHPB-10 aromatic parts are also different in the two solvents.

Spectra of BPBH-10 samples after drying of the solvent

ATR-FTIR spectra of the dry samples of thin films of BHPB-10 with various preparation history are shown in Fig. S-2. Most of these films have spectra similar to the BHPB-10 solution in cyclohexane (i.e. with NH and CO linked in the manner recorded for the self-assembling tubes normally formed in cyclohexane, cf. peaks (1550, 1599, 1612, 1715, 1725 cm⁻¹) with the red lines in Fig. S-1).



Fig. S-2 FTIR spectra of BHPB-10 dried films received from drop casting of BHPB-10/cyclohexanone solutions on various surfaces (from top to bottom): a wet film of a 1 wt. % solution of *ca.* 3 μ m thickness was squeezed between the diamond crystal and the clamp of the ATR accessory and then dried for 60 minutes (the spectrum remained unchanged after 30 minutes of drying); a film of *ca.* 50 μ m of a 0.2 wt. % solution cast on a PE plate and dried at ambient conditions for 6 hours (ATR); the same film after drying in vacuum (1 mbar) for additional 12 hours; the same films dried for 7 additional days at ambient conditions; PE plate alone (black line); film of *ca.* 500 μ m of a 0.2 wt.

% solution dried on a NaCl plate for 2 hours under vacuum (transmission spectrum); pure cyclohexanone (shown for comparison, orange line). (a) NH stretching region; (b) CO stretching region.

The spectra from the film cast from 0.2 wt% solutions on PE and dried 6 hours at ambient conditions show an additional peak at 1701 cm⁻¹. It decreased after 12 hours of drying in vacuum and eventually disappeared after long drying times. The origin of this peak is uncertain and may correspond to a shifted CO stretching mode of the CO of the cyclohexanone. The shift relative to the bulk solution can be attributed to an H-bond between the amide and the solvent. This demonstrates the extreme affinity of the cyclohexanone molecules to BHPB-10, which can destroy intra-BHPB hydrogen bonding even at very low concentrations of cyclohexanone (cf. the model of Fig. 5c-d).

When the film was observed by ATR using smaller amount of materials and dried in air, two additional features became visible. The spectrum recorded from the ultra thin film (from a film of ca. 3mm "wet" thickness of a 1 wt.% solution, after drying) formed on the diamond crystal showed all features observed for nanotubes (in BHPB-10 solution in cyclohexane) and two additional distinctly different features. The first one is a peak at 1595 cm⁻¹. Like for films on PE, it can correspond to the CO stretching of residual cyclohexanone (especially because the film was dried under vacuum). This mode was shifted to a lower frequency than in the bulk solution and thus suggests an H-bond between the ketone and the amide. The second feature is a shoulder at 1537 cm⁻¹. This shoulder was absent in films deposited on PE, even when the film was not fully dried. It

can be attributed to another amide II mode, and close to the frequency of the amide II in solution in cyclohexanone (1539 cm⁻¹). One should note that the amount of the BHPB material in the latter ultra thin film corresponds to relatively low number (5-7) of ~3 nm nanoribbon sub-layers, hence the ordering impact on nano-ribbon formation (described in Fig. 5 and the text before it) was not completely lost. On the contrary, in the films made from larger amount of BHPB material (e.g. a 50 μ m wet film of 0.2 wt. % solution corresponds to few dozens of nanoribbon sublayers), the formation of self-assembling structures took place in the whole volume (and not necessarily only near the surface), after cyclohexanone evaporation. In this case, no tendency to preserve the flat geometry (parallel to the surface) should be expected, hence nanotubes were formed.

The aromatic CC stretching modes show two distinct maxima at 1599 and 1612 cm⁻¹ and CO stretching modes with distinct maxima at 1715 and 1725 cm⁻¹. We had previously shown¹ that BHPB-n analogues forming nanotubes usually exhibit double frequencies for these modes, whereas BHPB-n analogues forming only ribbons exhibit single frequencies for these modes. In addition, BHPB-10 in toluene forms ribbons and also show a single frequency for the esters. The double frequencies of these modes are thus characteristic of nanotubular structure.

S-2. Mesomorphism of BHPB-10 structures in various situations

Solution of BHPB-10 in cyclohexanone at 0.05 mg/ml was deposited on a carbon-coated TEM grid, and the solvent was allowed to evaporate. On these grids, flat tapes with variable widths and exhibiting parallel striations were observed, suggesting that they were composed of thinner ribbons, as observed by AFM, Fig. S-3a (see also Fig. 4e). From these images, it became clear that the structures were flat (i.e., they did not have a tube-like shapes).

The tubular shape of the self-assemblies in cyclohexane was confirmed by freeze-fracture TEM. The observed replica allows to watch the fractured sample in relief, by the shadowing technique. Especially, at some spots, the ends of the tubes were visible, and clearly exhibited a hollow section (see Fig. 2d and Fig. S-3b). Meso-structures formed after drop-casting of a 50 μ m thick wet layer of BHPB-10 cyclohexanone solution (0.02 mg/ml) on Si wafer: they looked like wide bands, which were split into nanoribbons (Fig. S-3c).

By exposure of nanotubes to cyclohexanone, one can switch nanotubes back to nanoribbons. To a cyclohexane solution of BHPB-10 (which contained nanotubes), we added the same amount of cyclohexanone. Cyclohexanone destroyed the H-bonds and the π - π interactions between BHPB-10, causing the disassembly of the nanotubes. Drop-casting a mixed cyclohexanone/cyclohexane solution onto the substrate led to the self-assembly of BHPB-10 molecules into nanoribbons, see Fig. S-3d (cf. with structures in Fig. 4).



Fig. S-3 (a) Large-scale TEM image of drop-casted cyclohexanone BHPB-10 solution (0.05 mg/ml) on a carbon coated grid (after tungsten coating of the dried deposit). (b) Freeze-fracture of BHPB10 in cyclohexane (1 wt. %). Arrows: end of the aggregates showing their hollow section and tubular shape. (c) Large-scale AFM phase image of nanoribbons formed after drop-casting cyclohexanone BHPB-10 solution (0.02 mg/ml) on Si wafer. (d) AFM phase and topographic images of nanoribbons formed after drop-casting cyclohexanone and then drop casted on Si substrate.

S-3. BHPB-n tube geometry as a function of the tail length

The dependence of the self-assembled tube diameter on the length of the alkyl tail in cyclohexane solutions of BHPB-n was measured in ref. 1, the corresponding data are presented in Fig.S-4. The analysis of TEM images gives values for the external diameters of the aggregates. The tube wall thickness and the radius of the hollow space inside the tubes were measured by SANS analysis for each BHPB-n solution via a two-phase model (hollow long straight cylinder). The tube wall thickness proved to be 3.3 - 3.6 nm for all BHPB-n, $8 \le n \le 12$, and this value fits well to the model of single-layer tube (Fig.2e-f) where the wall thickness corresponds to the BHPB-n stretched molecule length. One should note that the model of homogeneous hollow cylinder is only a rough replica of the structure Fig.2e, where two distinct types of SIG sub-layers are present. However, without knowledge of the contrasts of the corresponding sub-layers, it is difficult to predict the direction to which the measured values of tube (wall thickness and diameter) would change, if one use Fig. 2e for fittings.

As a general conclusion from the data of Fig.S-4, we conclude that the average tube diameter increases with n. If the tube wall is organized as in Fig.2e-f (the n-tails are on the inner side of the tube wall), then the longer n-tails make the inner layer more bulky and resistant to compression (which inevitably takes place when the wall in curved into a tube). Thus, the longer is the n-tail, the less curved is the tube wall, and hence the larger is the tube diameter, in full accordance with Fig.S-4. In the opposite situation, if the n-tails were on the outer side of the tube wall (i.e. when the layer Fig.2e were inverted in the wall), the longer n-tails would make the outer part of the wall more swollen, hence

the tube diameter would be smaller for longer n-tails. This expected tendency contradicts to the measured data shown in Fig.S-4.



Fig. S-4 The average diameter of BHPB-n self-assembled nanotubes in cyclohexane increases with increase of the number (n) of carbon atoms in alkyl tail. Black squares: **external** diameters derived from a TEM image analysis (Table 1 of ref.1), red dots: **inner** diameters derived from SANS data, blue triangles: **outer** diameters derived from SANS data (Table 2 of ref.1).

S-4. Deposition vs. annealing

Temperature enhanced solvent vapor annealing (TESVA) makes tubes longer and better oriented on the surface, while their diameter stays approximately constant.



Fig. S-5 AFM images, comparing various BHPB-10 tubes: (a, b) nanotubes formed in solution and deposited by spin-coating from cyclohexane forming non-uniform bundles. (c, d) Tubes after annealing in cyclohexane vapor (starting from (a)). (e) Large scale image of better oriented nanotubes with a length up to micrometer, formed after annealing nanoribbons in cyclohexane vapor (starting from ribbons, Fig. 4). (f) Small scale topographic and phase images of nanotubes formed from nanoribbons after annealing in cyclohexane, showing their well defined homogeneous diameter and an open end (encircled) of a broken nanotube.

S-5. All-atomic computer modeling of self-assembled aggregates of SIGs

All-atomic modelling was performed using various tools incorporated in the commercial package HyperChem (TM) Release 7.5 for Windows. The geometrical optimizations of molecules and their ensembles were performed in vacuum at T=0K using the Amber96 molecular mechanics algorithm (with all components included, and both default Amber's 1-4 factors equal to 0.5). Dielectric constant was equal to unity. The termination condition was that the RMS gradient must fall below 1 kcal/(nm·mol).

The self-assembling structures formed by BHPB molecules are stabilized by strong attraction between SIGs of two distinct types: aromatic-ester rings (II) and amides (IV), see Fig. S-6. In order to clarify the physics of this stabilization, we performed minimization of two-dimensional layers made of model molecules similar to such SIGs, separately for the rings and for the amides. We evaluated the specific areas *S* and the specific energies *E* of such two-dimensional layers. The results are illustrated in Fig. S-7, S-8.

Both types of 2D sub-layers (made of ring or of amide groups) are quite stable, see the values of specific energies. We note also that specific areas per one ring group, per one amide group in longitudinal orientation and for two amide groups in transverse orientation are all close to $S=0.3 \text{ nm}^2$, making possible the formation of single and double lamellae as in Fig. S-6(b,c) (with corresponding orientations of SIGs). One should take into consideration that the values mentioned above are determined by minimization corresponding to zero temperature and to perfect alignment of SIGs, while the real

specific areas should be larger because of temperature expansion effect and due to entropic repulsion between the alkyl tails (I,III,V).

If the 2D layers are split into tapes, the edge energies for the amide sub-layer is strongly anisotropic, while the ring sub-layer has low edge energy in all directions (Fig. S-9). Hence, the total lamella structure will split preferably along the H-bond direction in the amide sub-layer.

In the slaty structures Fig. S-6(b,c) the orientations of both types of SIGs should necessary be parallel to the layers (Fig. S-10a). In particular, H-bonds in the amide layer should be horizontal (parallel to the sub-layer) as well. This condition translates into rotation of amide groups into either direction. Because they form a common amide sub-layer (where all amide SIGs should be parallel), the rotation should be into the same direction for all amide groups, hence spontaneous symmetry breaking should take place. The optimal rotation angle between the amide and the ring sub-layers should be around 60° in accordance with our molecular modeling Fig. S-10c.



Fig. S-6 The bisamide-ester gelator molecule BHPB-10 (a) and principle slaty layered structures made of them: single (red-green sandwich) (b) and double (with equivalent sides) (c) lamellae which are expected to be formed by such surfactants. In scheme (a) the standard chemical color code is used for atoms. In (b-c), the green color is used for SIG(II) (aromatic-ester rings), the red one for SIG(IV) (amide groups), and the sky-blue color is used for alkyl subchains (I,III,V).



Fig. S-7 The 2D arrangements of SIG(IV) groups (front and side views) and their specific characteristics (specific area *S* and energy *E* per one amide group). (a) The longitudinal amide sub-layer which has maximum specific area *S*. (b) The transverse amide sub-layer with minimum *S*. They are the typical arrangements for double lamella structure (Fig. S-6c) and for single lamella structure (Fig. S-6b), respectively.



Fig. S-8 The 2D arrangements of SIG(II) groups (front and side views) and their specific characteristics (specific area *S* and energy *E* per one ring group). The parallel (a) and antiparallel (b) ring sub-layers which are the typical arrangements for single lamella structure (Fig. S-6b) and for double lamella structure (Fig. S-6c), respectively.



Fig. S-9 The edge energies in 2D sub-layers made of amide and ring SIGs. (a) In amide sub-layer the easy splitting direction (shown with blue dashed line) goes parallel to H-bonds. (b) In ring sub-layer all direction are easy enough for splitting.



Fig. S-10 On the origin of spontaneous chirality of the self-assembling structures in BHPB systems. (a) In the single molecule ground state (shown) the amide dipoles are not parallel to the future amide sub-layer (red horizontal line). The easiest way to make the dipole horizontal is to rotate it by twisting the alkyl spacer C₅H₁₀. (b) The dipole SIGs align to their sub-layer, but they become not parallel to the planes of the ring SIGs. The chirality is defined by the sign of the angle α (right or left). (c) The optimal positions of the pairs of amide groups (belonging to the same BHPB molecule (as in (a)) and involved into the shown amide sub-layer) connected to a ring SIG with a fixed orientation (shown with black dotted line). The total twist energies ε are indicated by color, apparently the most favorable configuration corresponds to 60⁰ rotation.

S-6. Estimating specific width of a nanoribbon

In the main text we proposed a model for the nanoribbons that are formed during the drop casting of BPBP-10 cyclohexanone solution on Si wafers (see Fig. 4,5 and Eq.1-4 in the main text). Quadratic expansion for the main terms of the free energy that describes the thin lamellar layer stabilized by two distinct types of SIG-based sublayers is given by Eq.1.

The green SIG sub-layer (made of aromatic SIGs) has a fixed surface density which is characterized with specific area S_1 ; the aromatic groups are assumed to form strong compact sub-layer that stabilizes the lamella. The red SIG sub-layer (made of amide groups initially solvated with the solvent molecules) if taken alone is characterized by specific area $S_2^{(0)}$ that changes during the drying process. At the beginning of the drying process $S_2^{(0)}\approx S_1$, and at the end of it: $S_2^{(0)}\approx S_2^{(dry)}$, where $S_2^{(dry)}$ is the specific area of dry amide sub-layer ($S_2^{(dry)} < S_1$). In the red-green-red lamella the amide sub-layers are stretched, hence they have specific area S_2 that in general case does not coincide with the current $S_2^{(0)}$ corresponding to the free amide sub-layer with given current cyclohexanone contents. Apparently $S_2^{(0)} < S_2 < S_1$, the difference between $S_2^{(0)}$ and S_2 is paid by the stretching energy of the amide sub-layers, and the difference between S_2 and S_1 is on the cost of deformation of the alkyl spacers that connect the ring and the amides sub-layers, see Fig. 5e. For quadratic expansion of Eq.1 all deformations are assumed to be low enough. If the layer is coherent (no cracking), $S_2=S_1$ and $w^{-1}=0$, this is a case when only the second term is present in the free energy Eq.1. The elasticity κ is a stretching characteristic of the amide sub-layer alone (at the given stage of the drying process). In the cracked layer: S_2 can be lower (closer to $S_2^{(0)}$), in this case the amide sub-layer stretching energy decreases on the cost of the edge energy of the cracks and of the stretching energy of the alkyl spacers (the first and the third terms of Eq.1, respectively). One should note that all three terms in Eq.1 come from physically different areas of the lamella in question. The first term in Eq.1 comes from the physical breaks in the amide sub-layer, it characterizes the tape *edges*. The second term characterizes the stretching ability of the amide sub-layer, it comes from the *total area* of the amide sub-layers (we assumed homogeneous stretching in Eq.1), one can imagine such stretching as the amide group rotation from the optimal transverse orientation Fig. S-7b to something more close to Fig. S-7a. The last term in Eq.1 comes from *alkyl spacers*: when the specific areas in the two types of SIG sub-layers do not coincide $(S_2 \neq S_1)$, the sub-layers should be mutually shifted (more strongly near the edges of the tapes, see Fig. 5e: the relative shift is $\sim w(S_1-S_2)/(2S_1)$ near the tape edges), hence the sub-chains that join the red and the green SIGs should be stretched; in accordance to Gaussian model of polymers, this stretching energy is inversely proportional to the length of the alkyl spacers.

Our scaling analysis of the lamella free energy (see the main text) shows that for strong mismatch between the layers, the tape width w (Eq.4) is determined by the competition between the first and the last terms in Eq.1. Here we make estimation for equilibrium

tape width w in this regime taking into account some physical values known for the BHPB-10 molecules.

The alkyl spacer is made of m=5 CH₂ groups. For each group, the typical step in planar direction (along the plane parallel to the SIG sub-layers) is $b\sim1\text{\AA}$, hence the typical size of the spacer in planar direction is $R_{//2} \sim mb^2 \sim 5\text{\AA}^2$. Now we construct the first and the last terms of Eq.1.

Consider a linear fragment of length a of the ribbon made of lamella like in Fig. 5e (of width w). The energy corresponding to the first term of Eq.1 is

$$E_1 = \gamma \alpha$$
 (A.1)

here γ corresponds to *both* edges of the ribbon (hence $\gamma \sim 2kT/Å$ for the situation shown by the blue line in Fig. S-9a).

The number of chains in the fragment is N = aw/S. The number of spacers is twice larger. Their total spacer's elastic energy (corresponding to the last term in Eq. 1) is (per spacer):

$$\frac{E_2}{2N} = kT \frac{R_x^2}{2mb^2} \tag{A.2}$$

where m = 5 is the spacer length, Rx is the lateral deformation and "b" is as determined above.

The lateral deformation Rx changes from zero (in the center of the tape) to $(w/2)(\delta S/S)$ (on its edge), then

$$\left\langle R_{x}^{2}\right\rangle = \frac{R_{x,\max}^{2}}{3} = \frac{w^{2}}{12} \left(\frac{\delta S}{S}\right)^{2}$$

Hence,

$$E_2 = kTN \; \frac{\left\langle R_x^2 \right\rangle}{mb^2} = \frac{aw^3}{12} \frac{kT}{mb^2 S} \left(\frac{\delta S}{S}\right)^2 \tag{A.3}$$

Minimization of $(E_1 + E_2)/N$ gives analogue of Eq. 4:

$$w^{3} = 6\gamma S \frac{mb^{2}}{kT} \left(\frac{S}{\delta S}\right)^{2}$$
(A.4)

If we use $\gamma = 2 \text{ kT/Å}$, m = 5, $S = 30 \text{ Å}^2$, $\delta S = 1 \text{ Å}^2$, $b \sim 1 \text{ Å}$ (arbitrary value), then Eq. A.4 gives $w \sim 120 \text{ Å}$ which is in agreement with our experimental results Fig. 4.

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