Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Perturbation induced formation of a 3D-network of microcrystals producing soft materials.

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Chemicals. bTbk was obtained as described in reference number 1 and purified by flash chromatography on silica gel to avoid possible gelation induced by impurities.[i] Elemental analysis: Found (calculated) **bTbk**, C 62.79 (62.70), H 9.37 (9.15), N 6.19 (6.36). Toluene and 1-chloronaphtalene (ACS reagent).

Elemental analysis. Analyses were performed using a Flash EA analyser, 1112 series Thermo Finnigan driven by the Eager 300 software (oven temperature: 970°C, gas: helium, flow rate: 140 mL/min, detector: catharometer).

Crystal growth. The toluene solvates were obtained from **bTbk** solutions (10 mg) in 10 mL.

Powder X ray diffraction. XRD (X-ray diffraction) patterns on powders, crystals or gels were recorded on a Siemens D500R XRD diffractometer using Cu Kα radiation in the 5-40° 2θ range with a 0.04° step associated with a step time of 1s.

Gelation experiments. All gelation tests were performed using 28.2 mg of **bTbk** in 400 μL of solvent (except when found particularly soluble, in these cases the concentration was doubled). The capped vials were heated to approximately 80°C followed by immersion to the ultrasound bath (Labo Moderne, Sonoclean, 35 kHz, 2×160 W, 0.95 W.cm^{-2}) for various durations. The gelation was simply confirmed by inverting the vial and checking that the immobilized solution did not flow. The stirring and shaking experiments were performed at a concentration of 120 mM in toluene. In each case, the **bTbk** suspension was first heated to ~100°C prior to (i) stirring with a spatula for ~2 seconds in an ice bath (3°C) until gels formed, (ii) stirring with an included magnetic stirrer for ~4 seconds in an ice bath again until gels formed and (iii) shaking for 5 seconds in an ice bath.

EPR spectroscopy. The crystal EPR measurements were performed on a BRUKER EMX spectrometer operating at 9.4 GHz (X-band). The spectrometer was equipped with a goniometer which allowed us to select a precise orientation for the sample. The liquid and gel EPR measurements were performed on a BRUKER Elexsys and EMX spectrometers operating at 9.4 GHz (X-band) in 50 μL capillaries using the following parameters: microwave power 5 mW and modulation amplitude 0.1 G.

Scanning Electron Microscopy. Micron scale images were acquired on a Hitachi S-4800 Cold Field Emission Scanning Electron Microscope (SEM). This instrument was fitted with two secondary detectors and images were acquired using a mixed image of the two signals at a working distance of 8 mm. Images were acquired at a beam energy of 2 keV and a current of 5 μA. The dry materials were deposited onto aluminium stubs on adhesive carbon tapes. However, this technique under high vacuum did not preserve the texture of the gel and we could only see collapsed structure (highly disordered polycrystalline phase) and this is the reason why we used cryo-SEM (see below).

Cryo-Scanning Electron Microscopy. Samples preparation: 16 mg of **bTbk** were weighted in a vial prior to addition of 300 μL of toluene (120 mM). Each sample was prepared by rapidly solubilizing the molecule at ~100°C followed by applying the relevant stimulus during cooling in an ice bath (3°C) until the solution set as a gel or a viscous liquid. For manual stirring, a spatula was simply allowed to gently stir the toluene solution for around 2 seconds. For magnetic stirring, a magnetic stirrer was introduced inside the vial allowing the solution to gently stir for around 5 seconds. For shaking, the vial was simply circularly shaken for around 6 seconds at 3°C. For ultrasound, the vial was introduced in a Branson 2510 ultrasound cleaner device for around 20 seconds. Small portions of gels or gelly materials were deposited on an aluminium sample holder and rapidly freezed at -196°C in liquid nitrogen (this allowed to image the micromorphology *in the gel state* since the solvent is still present during the analysis). After ~ 1 minute, the samples were tranfered to a vacuum chamber (T = -196°C, P = 10^{-5} Pa) before depositing a thin layer of a Au/Pt alloy. The samples were then introduced in a Cryo OXFORD Alto 2500 platine (T = -196°C under vacuum) and imaged using a Philips XL30 SFEG scanning electron microscope. Elemental analysis was performed to confirm the presence of carbon and oxygen *in situ* using an EDS OXFORD INCA 300 spectrometer.

Table S1. **Effect of concentration and sonication time on supramolecular gelation.**

(**S**: solution, **I**: insoluble, **PG**: partial gel, **GEL**: gel, **C**: crystals; 400 μL total volume).

Entry	Solvent	Heat/Cool	US 05'	US 10'	US 15'	US 20'	US 30'	US 45'	US 60'	Heat/Cool
01	20 mM	S	S	S	S	S	S	S	S	S
02	30 mM	S	S	S	S	S	I	S	S	S
03	40 mM	S	**C**	**C**	**C**	**C**	S	I	I	S
04	50 mM	**C**	**C**	**C**	**C**	**C**	PG	I	I	S
05	60 mM	**C**	C/PG	**C**	**C**	PG	PG	PG	I	**C**
06	70 mM	**C**	C/PG	**C**	C/PG	PG	PG	PG	**C**	**C**
07	80 mM	**C**	C/PG	**GEL**	**GEL**	**GEL**	C/PG	PG	PG	**C**
08	90 mM	**C**	C/PG	**C**	**GEL**	C/PG	**GEL**	PG	PG	**C**
09	100 mM	**C**	C/PG	C/PG	C/PG	PG	**GEL**	PG	PG	**C**
10	110 mM	**C**	C/PG	C/PG	**GEL**	PG	**GEL**	**GEL**	PG	**C**
11	120 mM	**C**	**GEL**	**GEL**	**GEL**	**GEL**	**GEL**	PG	PG	**C**
12	130 mM	**C**	C/PG	**GEL**	**GEL**	**GEL**	**GEL**	PG	**GEL**	**C**
13	140 mM	**C**	**GEL**	**GEL**	**GEL**	**GEL**	PG	PG	PG	**C**

Table S2. **Solvents tested for gelation with bTbk using ultrasound.**

(**S**: solution, **I**: insoluble, **PG**: partial gel, **G**: gel, **C**: crystals).

Molecule	Solvent	Status	Molecule	Solvent	Status
1	Water (20 mM)	**I**	***2***	Water (120 mM)	**I**
1	Ethanol (320 mM)	**C**	***2***	Methanol (120 mM)	**S**
1	Acetonitrile (320 mM)	**S**	***2***	Acetonitrile (120 mM)	**S**
1	DMF (320 mM)	**S**	***2***	DMF (120 mM)	**S**
1	DMSO (320 mM)	**S**	***2***	AcOEt (120 mM)	**S**
1	AcOEt (160 mM)	**I**	***2***	Et_2O (120 mM)	**I**
1	Et_2O (160 mM)	**I**	***2***	Acetone (120 mM)	**S**
1	Acetone (320 mM)	**S**	***2***	$CHCl_3$ (120 mM)	**S**
1	$CHCl_3$ (320 mM)	**S**	***2***	n-Hexane (120 mM)	**I**
1	Pyridine (320 mM)	**S**	***2***	Toluene (120 mM)	**S**
1	Hexane (160 mM)	**I**			
1	Cyclohexane (160 mM)	**PG**			
1	1-chloronaphthalene (160)	**G (C)**			

* in the case of molecule 2, the results are that of visual inspections after applying a heating and cooling cycle to a suspension of 12.4 mg in 250 μL of solvent. The outcome was identical when applying ultrasound during the cooling of hot solutions.

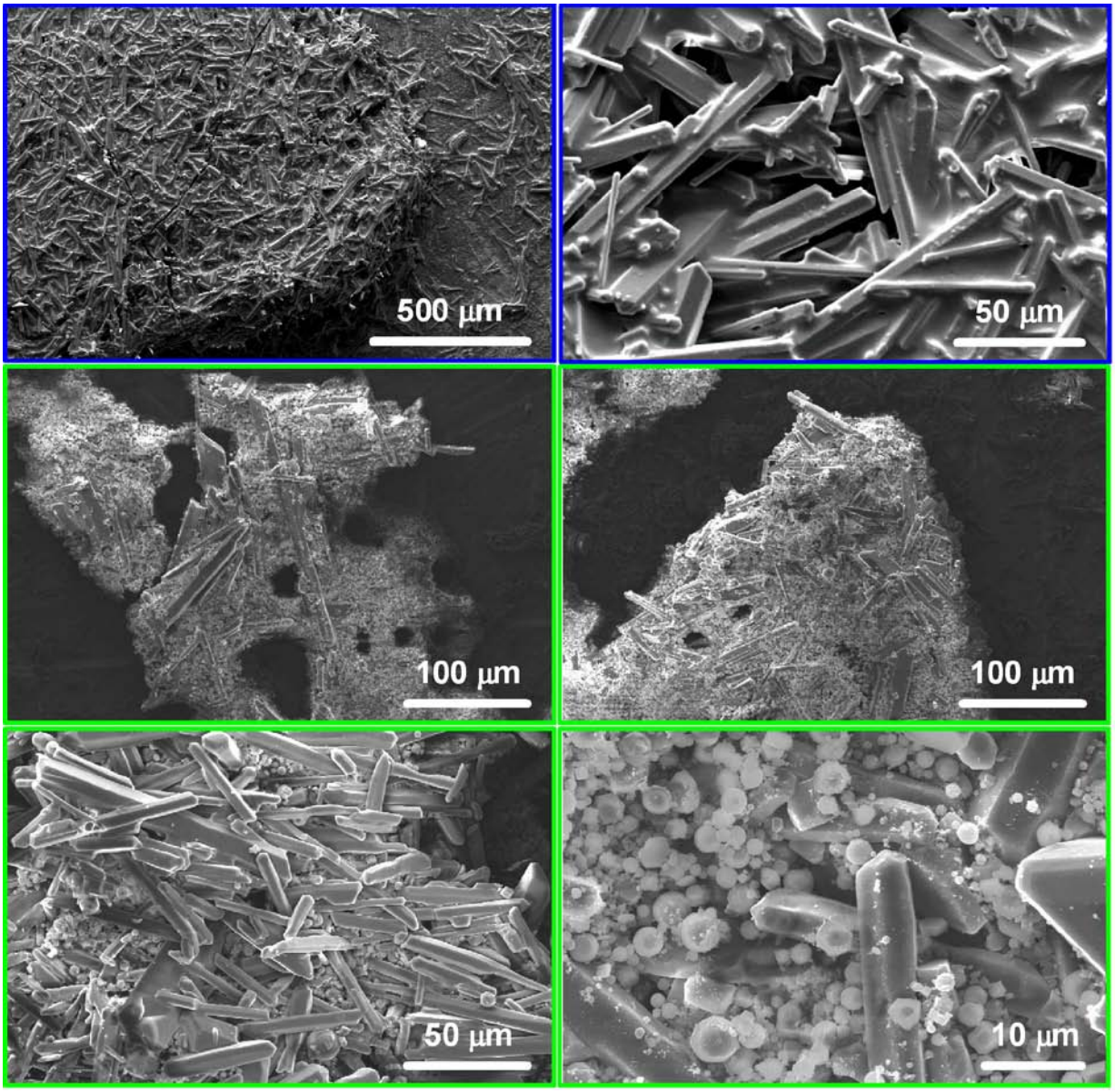

Figure S1. cryo-SEM micrographs of various areas of gel samples obtained (i) by *magnetically stirring* while cooling a supersaturated **bTbk** solution (120 mM) in toluene to 3°C (blue frames) and (ii) by submitting the sample to ultrasound (20 s) while cooling a supersaturated **bTbk** solution (120 mM) in toluene to 3°C (green frames).

Contrary to the cases of manual and magnetic stirring (Figure 2 of the paper), the cement which maintain the crystals together in the gels obtained using ultrasound (green frames) may be the stuck spheres which are seen at high magnifications.

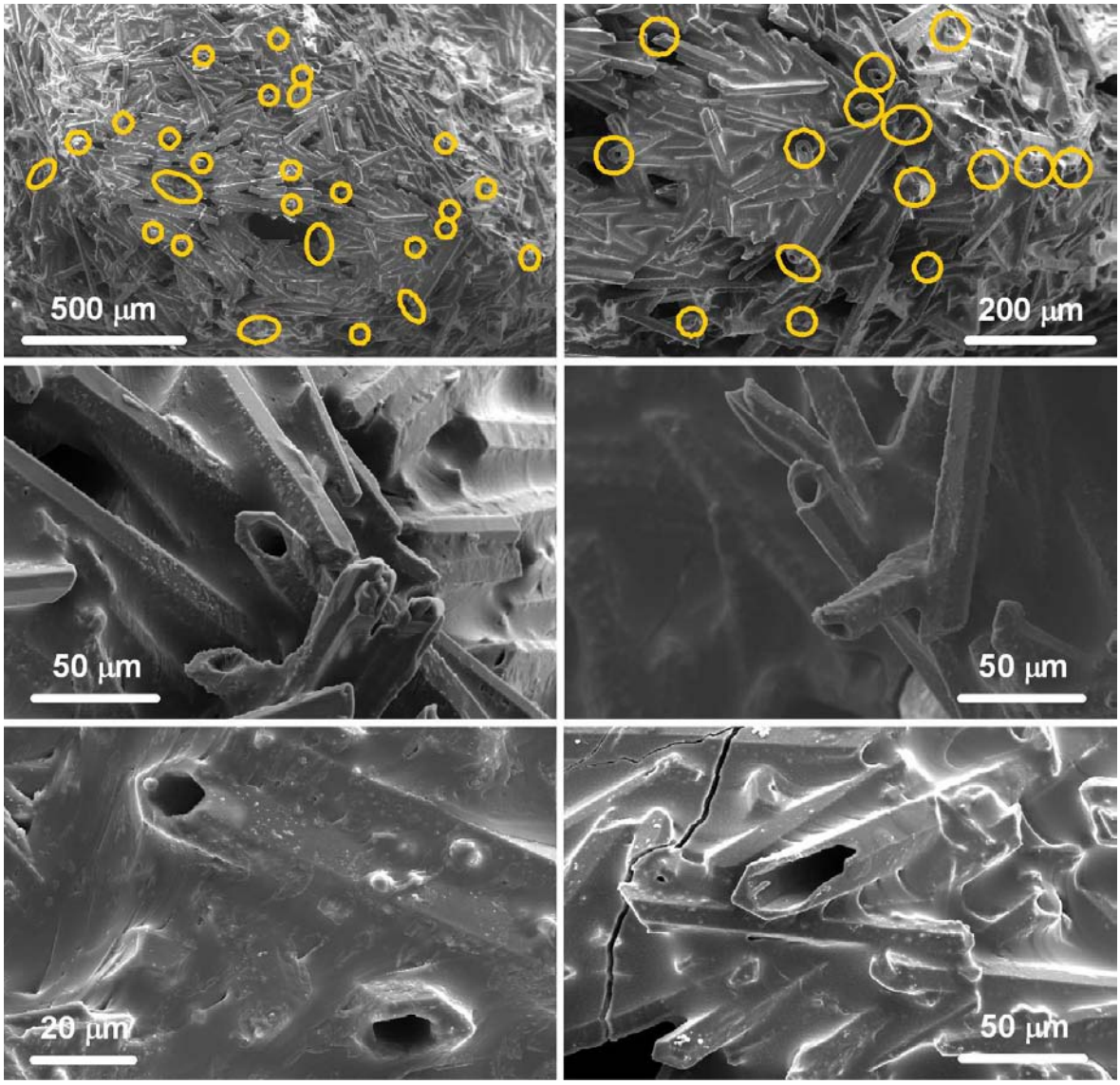

Figure S2. cryo-SEM micrographs of various areas of a viscous sample (gelly) obtained by circularly *shaking* while cooling a supersaturated **bTbk** solution (120 mM) in toluene to 3°C.

The orange circles represent the areas where hollow microtubes were identified.

[i] Y. Matsuki, T. Maly, O. Ouari, H. Karoui, F. Le Moigne, E. Rizzato, S. Lyubenova, J. Herzfeld, T. Prisner, P. Tordo, R. G. Griffin, *Angew. Chem., Int. Ed.* **2009**, *48*, 4996-5000.