Electronic Supplementary Information for

Box-like gel capsule from heterostructure based on a core-shell MOF as template of crystal crosslinking

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Experimental Section

Supplemental Figure

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Materials

Azbpdc[1] and tripropargylamine (**CL3N**)[2] were synthesized according to the reported procedures. All solvents and inorganic reagents were purchased from some commercial suppliers and were used without further purification. All experiments were carried out under ambient atmosphere. A dispersion of fluorescent microbeads (Fluoresbrite Plain Microsphere) was purchased from Polysciences, Inc.

Measurements

Fourier transform infrared (FT-IR) spectra were obtained on a JASCO FT/IR-4100 spectrometer. X-ray diffraction (XRD) patterns were obtained by using a Bruker D8Advance with Cu Kα radiation source (40 kV, 40mA). Optical micrographs were obtained by using a Nikon instruments SNZ1000 stereoscopic zoom microscope and Zeiss AxioCam ICc1. ^{1}H-NMR spectra were measured on a Bruker DRX-500MHz.. Scanning electron microscope (SEM) images were obtained by using a JEOL JIB-4600F/HKD.

X-ray Crystallography Analyses

Single-crystal of $\mathbf{[Zn_4O(Azbpdc)_3]_n}$ were mounted in the loop using paraffin oil. The data were collected on a Rigaku AFC-7R Mercury diffractometer with graphite monochromated Mo Kα radiation (0.71069 Å) and a rotating-anode generator operating at 50 kV and 200 mA. Diffraction data were collected and processed using the CrystalClear program.[3] Structures were solved by direct methods using SHELXS-97.[4] Structural refinements were conducted by the full-matrix least-squares method using SHELXH-97.[4] Non-H atoms were refined anisotropically, and H atoms were refined using the riding model. All calculations were performed using the Yadokari-XG software package.[5]

Preparation of Core (IRMOF-9) single crystals

The organic ligand **bpdc** (25 mg, 0.10 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (60 mg, 0.20 mmol) were dissolved in 5 mL of DMF in a screw top vial. The vial was kept standing at 80 °C for 3 days. The solution was decanted and cubic crystals were repeatedly washed with DMF.

Preparation of AzCS

Azbpdc (25 mg, 70 μmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (60 mg, 200 μmol) were dissolved in 1 mL of DMF in a hydrophobized screw top vial. The vial was kept standing at 80 °C for 1 days. Then several single crystals of IRMOF-9 were immersed in the mixture and heated for 6 hours additionally. The solution was decanted and cubic core-shell crystals were repeatedly washed with DMF.

Preparation of CLCS

250 μL of saturated CuBr solution was added to 0.1 M tripropargylamine / DMF solution in a screw top vial. The mixture was standing at 80 °C for 1 day. At that time, brownish precipitate was dispersed in the solution. Then **AzCS** was immersed in the mixture and standing at 80 °C for 7 days. The solution was decanted and cubic core-shell crystals were repeatedly washed with DMF.

Preparation of Box-gel

CLCS was immersed in a mixed solvent of 0.5 M H_2SO_4 / DMSO in a screw top vial. The vial was kept standing at room temperature for 1 day. The supernatant was decanted, and yellow polymer gels were repeatedly washed with DMF.

Preparation of single crystals of $[Zn_4O(Azbpdc)_3]_n$

Azbpdc (25 mg, 70 μmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (60 mg, 200 μmol) were dissolved in 1 mL of DMF in a screw top vial. The vial was kept standing at 80 °C for 5 days. The solution was decanted and cubic crystals were repeatedly washed with DMF.

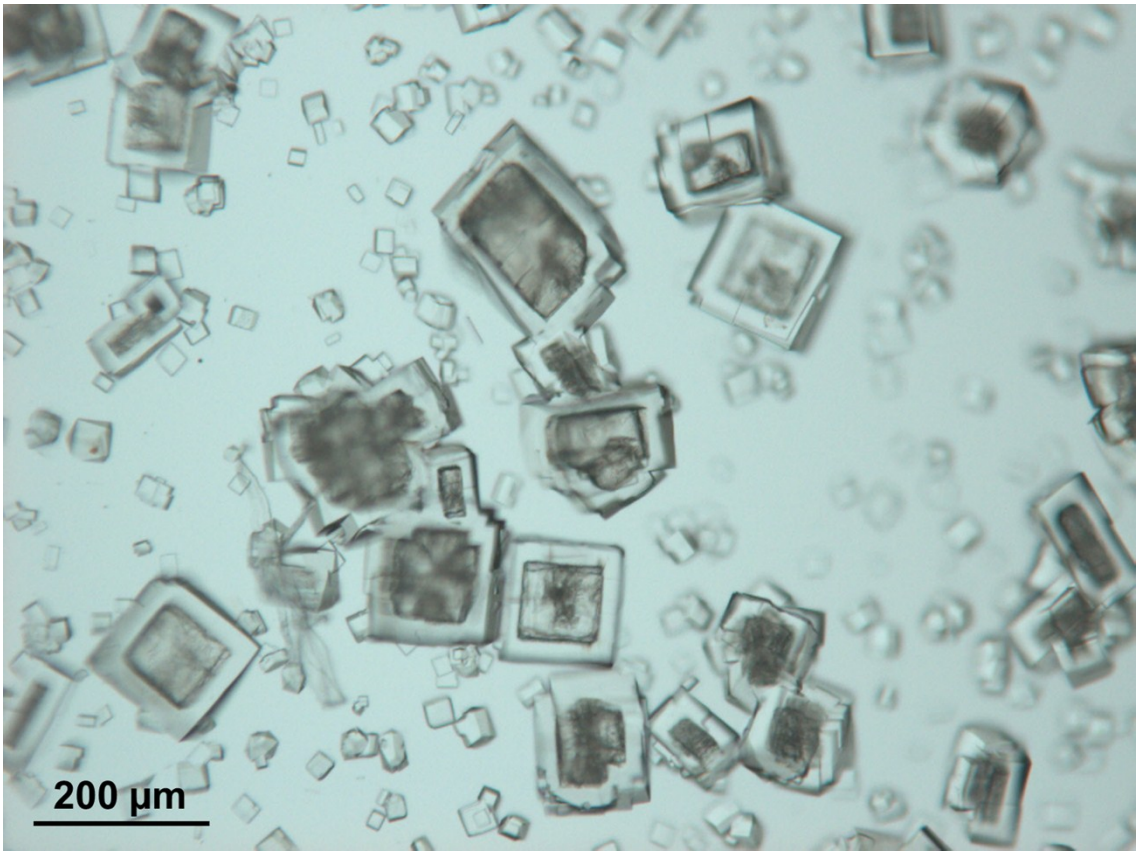

Fig. S1 A photograph of vial after preparation of **AzCS** (**$[Zn_4O(Azbpdc)_3]_n$** was manually removed).

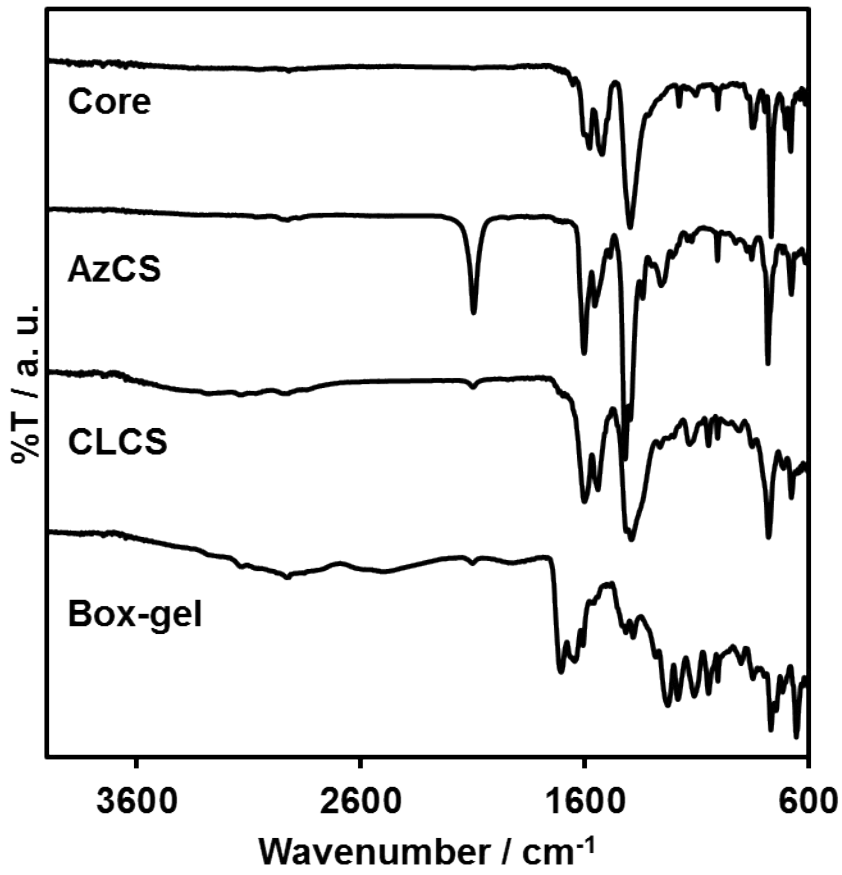

Fig. S2 FT-IR spectra of **Core**, **AzCS**, **CLCS** and **Box-gel**.

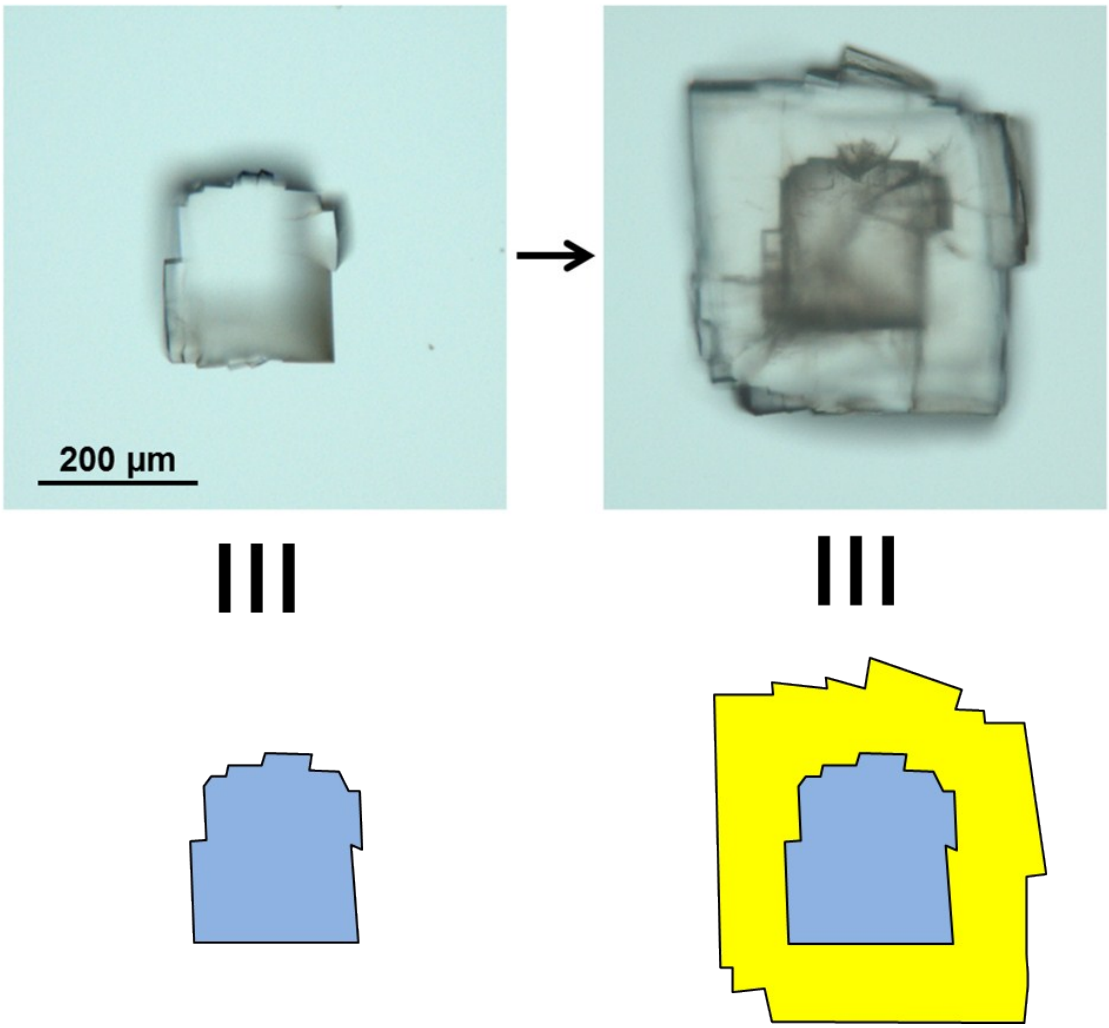

Fig. S3 Optical microscopy images of **Core** and **AzCS** with unique shape. The shape of core did not change and constructed shell had similar shape with **Core**.

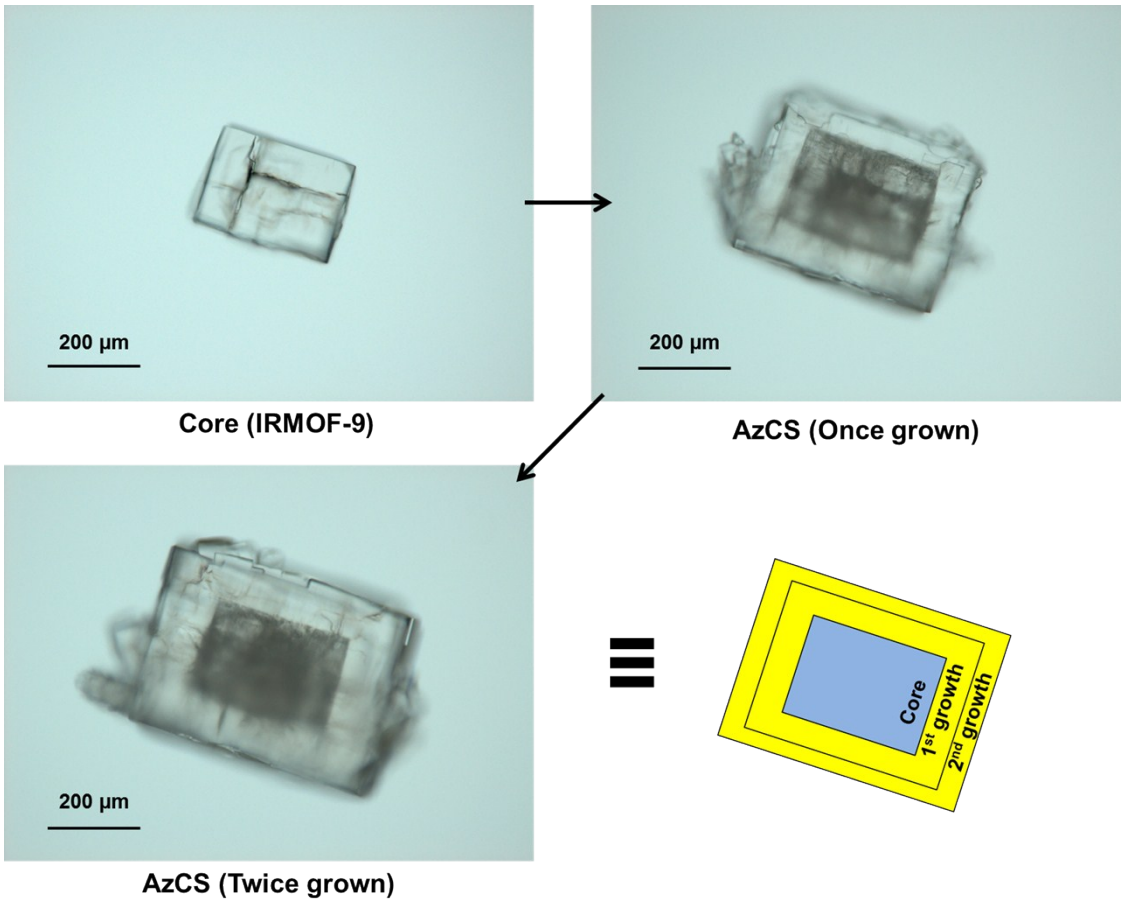

Fig. S4 Optical microscopy images of core and **AzCS**. The shell thickness was increased with times of epitaxial crystal growth.

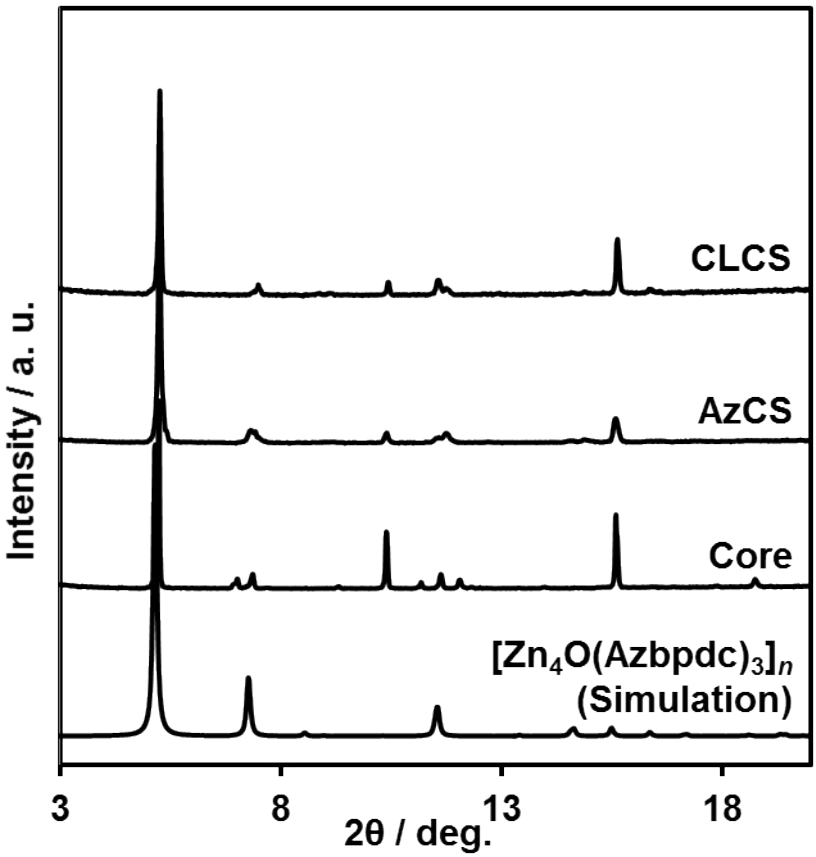

Fig. S5 XRD measurement of **Core**, **AzCS**, and **CLCS**.

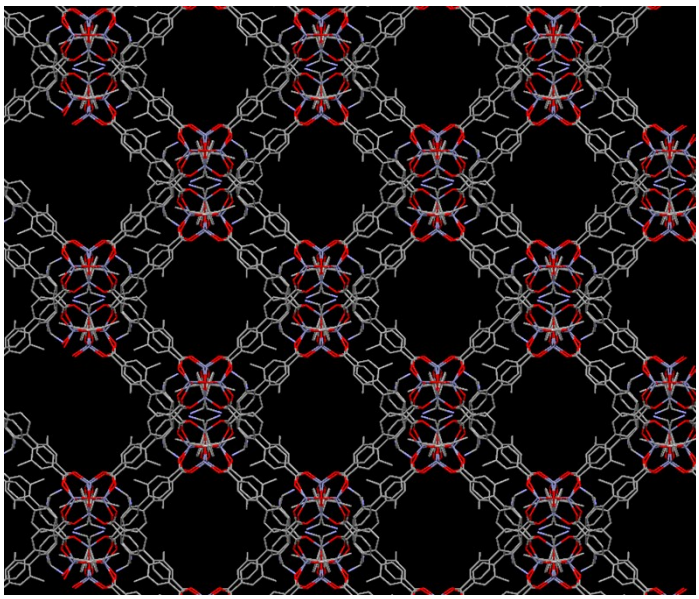

Fig. S6 Crystal structure of **$[Zn_4O(Azbpdc)_3]_n$** consisting of **Azbpdc** and Zn ions.

Table S1. Crystallographic data for **$[Zn_4O(Azbpdc)_3]_n$**.

Compounds	**$[Zn_4O(Azbpdc)_3]_n$**
Chemical formula	$C_{48}H_{30}N_{18}O_{15}Zn_4$
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimension	24.187(3) Å
	24.1807(13) Å
	24.292(2) Å
	59.829(5) deg.
	60.346(4) deg.
	60.346(4) deg.
	V = 10075.1(15) $Å^3$
Final *R* indices	R_1= 0.0791

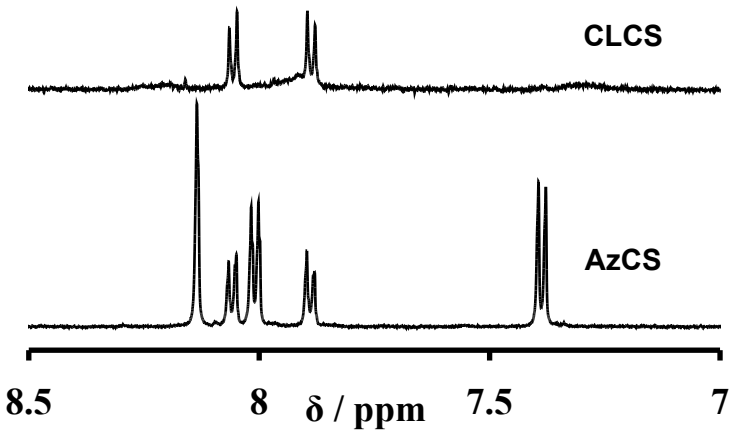

Fig. S7 ^{1}H-NMR spectra of **AzCS** and **CLCS** after digestion or extraction in D_2SO_4/DMSO-d_6.

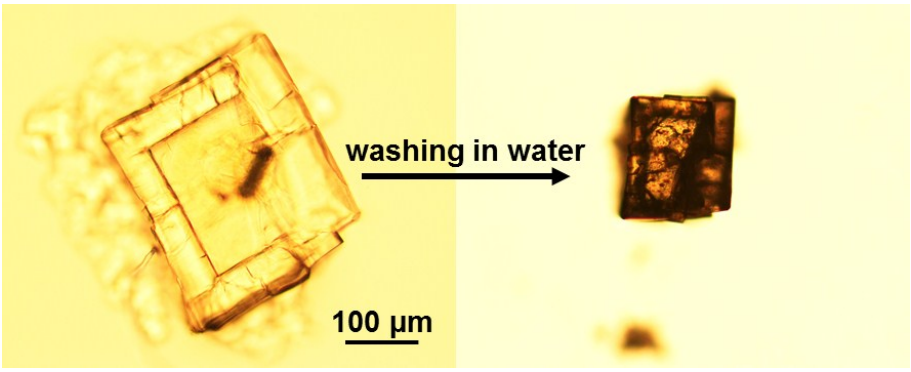

Fig. S8 Optical microscopy image of **Box-gel** shrunk in poor solvent (water).

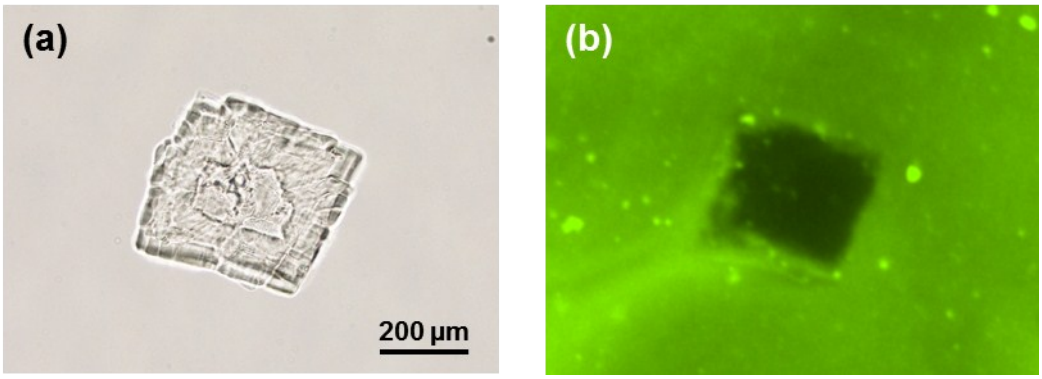

Fig. S9 (a) A photograph of **Box-gel** immersed in DMF and (b) a fluorescent micrograph of the **Box-gel** immersed in a dispersion of fluorescent microbeads (diameter: 0.5 μm) in DMF.

References

1. S. Nagata, H. Sato, K. Sugikawa, K. Kokado, K. Sada, *CrystEngComm* 2012, **14**, 4137–4141.

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3. *CrystalClear*; Molecular Structure Corp.: Orem, UT, 2001.

4. *SHELX-97*; G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, **64**, 112−122.

5. *Yadokari-XG*; Program for Crystal Structure Analysis. Wakita, K. 2000.