

***Supporting Information for***  
***Breath figure fabrication of honeycomb film with small***  
***molecules through hydrogen bond mediated***  
***self-assembly***

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## I. General Methods.

Chemicals and solvents were purchased and used as received unless otherwise indicated. All oxygen and moisture sensitive reactions were performed under nitrogen atmosphere using standard Schlenk technique. Reagent grade tetrahydrofuran (THF) and toluene were distilled from sodium and benzophenone. Triethylamine (TEA) was distilled from CaH<sub>2</sub> prior to use. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Varian Mercury 200 (200 MHz), Mercury plus 300 (300 MHz), Bruker Avance 400 (400 MHz) Nuclear Magnetic Resonance Spectrometer, using CDCl<sub>3</sub> as the solvent unless otherwise noted. Chemical shifts were reported in parts per million (ppm). <sup>1</sup>H NMR chemical shifts were referenced to TMS (0.0 ppm) and <sup>13</sup>C NMR chemical shifts were referenced to CDCl<sub>3</sub> (77.23 ppm) as standards. Absorption spectra were recorded on a PerkinElmer Lambda 35 UV-vis Spectrometer. Photoluminescence spectra were recorded on a PerkinElmer LS55 Luminescence Spectrometer. ESI mass spectra were obtained on a Bruker APEX IV mass spectrometer. Elemental analyses were performed using a German Vario EL III elemental analyzer.

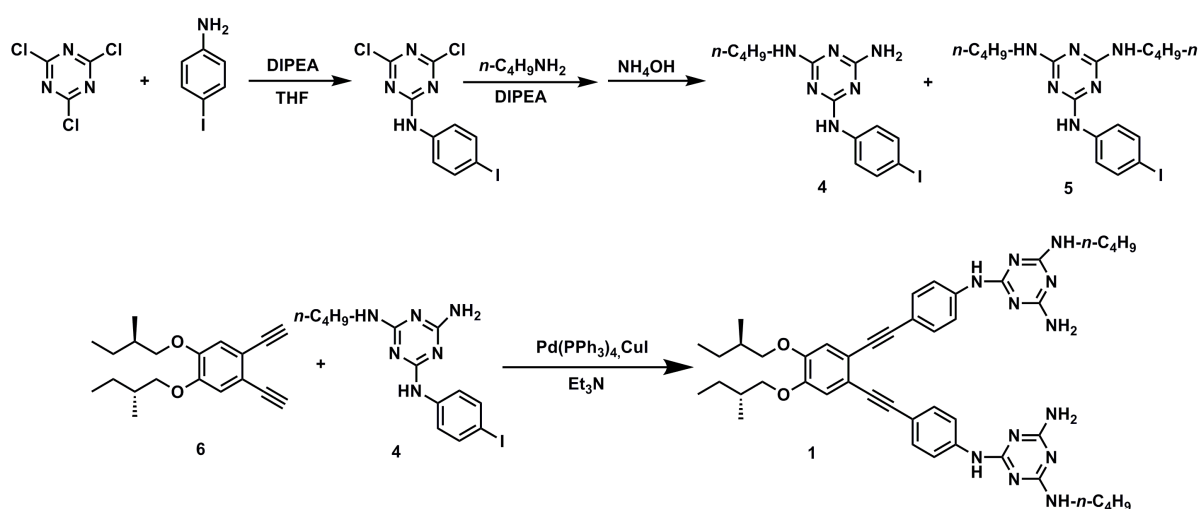
**Gelation Test.** A vial inversion test was taken under typical procedure as following: in a test vial, molecule **1** was mixed with appropriate amounts of solvent and the mixture was heated until the solid dissolved. The resulting clear solution was cooled to room temperature naturally. When the test vial could be inverted without changing the shape of its content, gel formation was indicated.

**Gel-Sol Transition Temperature (T<sub>gel</sub>) Measurement.** The T<sub>gel</sub> was determined by the ball-drop method: a test tube containing the gel was immersed inversely in a thermostat water bath. The T<sub>gel</sub> was defined as the temperature at which the gel began to flow with increasing temperature. The temperature was increased at a rate of 0.2 °C/min controlled by a PolyScience programmable temperature controller.

**CD Measurements.** The gelator and solvents were heated to achieve a clear solution and then the solution was dropped onto a piece of glass. The solution gelled while cooled in air. CD spectrum was recorded using a JASCO J-810 spectrometer.

**Two-dimensional (2D) WAXD.** The X-ray diffraction patterns of xerogel were obtained from a Bruker D8Discover diffractometer with GADDS as a 2D detector. Silicon powder and silver behenate were used as standards. The 2D diffraction patterns were recorded in a transmission mode at room temperature. For both powder 1D and 2D diffractions, the background scattering was recorded and subtracted from the sample patterns.

## II. Synthetic procedures

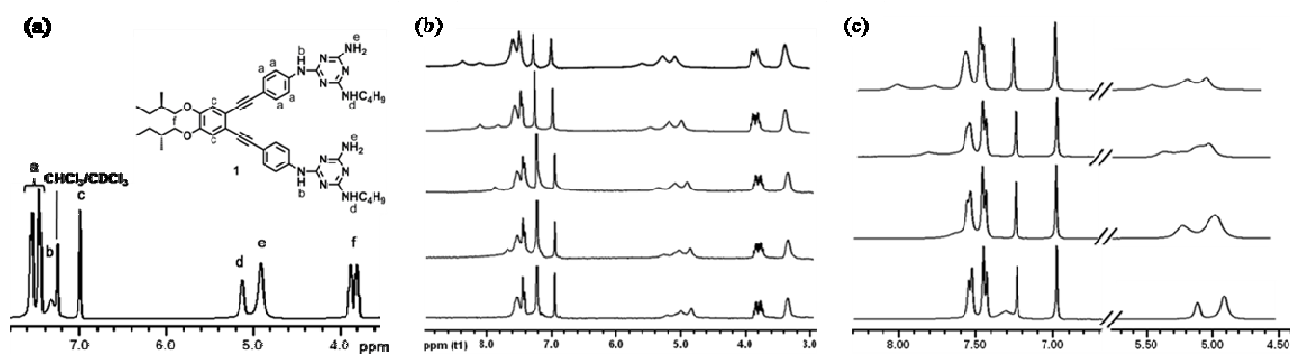


***N*<sup>2</sup>-butyl-*N*<sup>4</sup>-(4-iodophenyl)-1,3,5-triazine-2,4,6-triamine(4):** Procedure was similar to the literature<sup>[1]</sup>: a solution of cyanuric chloride (0.54 g, 3 mmol) was dissolved in freshly distilled THF (20 mL) and cooled in an ice-water bath. A THF solution (20 mL) of 1 equiv. of 4-iodoaniline (0.65 g, 3 mmol) and 1 equiv. of DIEA (*N,N*-diisopropylethylamine, 0.38 g, 3 mmol) was added *via* an additional funnel over the course of 15-30 min with magnetic stirring. The mixture was allowed to warm to room temperature after addition and stirred for another hour. The mixture was then cooled in an ice-water bath. Another equiv. of butylamine (0.21 g, 3 mmol) and 1 equiv. of DIEA (0.38 g, 3 mmol) were added with stirring and the mixture was stirred for 8 hours or until TLC showed no further change. The intermediate was used directly in the next step after filtering and removing solvent by rotary evaporation. The intermediate dissolved in 10 mL of freshly distilled THF and approximately 10 mL of 3%  $\text{NH}_4\text{OH}$  were placed in a 50 mL pressure bottle. The bottle was capped and heated (CAUTION. behind a safety shield) to 100-105°C in an oil bath for 10 h. The bottle was cooled and the solution was poured into 200 mL of  $\text{H}_2\text{O}$ . The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3×50 mL), and the organic phases were collected, washed with brine

(20 mL), dried over MgSO<sub>4</sub>. The crude melamine was purified by flash chromatography on silica gel (EtOAc/CH<sub>2</sub>Cl<sub>2</sub>, 1:5) to afford *N*<sup>2</sup>,*N*<sup>4</sup>-dibutyl-*N*<sup>6</sup>-(4-iodophenyl)-1,3,5-triazine-2,4,6-triamine (**5**), and then (MeOH/CH<sub>2</sub>Cl<sub>2</sub>, 1:20) to afford 1.08 g (94 %) of the desired product **4** as a white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.58 (d, *J* = 8.7 Hz, 2H, PhH), 7.35 (m, 2H, PhH), 6.80 (br, 2H, -*NHPh*), 5.00-4.70 (m, 3H, -*NH*-, -*NH*<sub>2</sub>), 3.38 (q, *J* = 7.2 Hz, 2H, -*NHCH*<sub>2</sub>*CH*<sub>2</sub>), 1.57 (m, 2H, -*CH*<sub>2</sub>*CH*<sub>2</sub>*CH*<sub>3</sub>), 1.41 (m, 2H, -*CH*<sub>2</sub>*CH*<sub>2</sub>*CH*<sub>3</sub>), 0.95 (t, *J* = 6.6 Hz, 3H, -*CH*<sub>3</sub>), <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 166.5, 166.1, 164.4, 139.1, 137.5, 122.2, 85.7, 40.7, 31.7, 20.1, 13.9; Anal. Calcd for C<sub>13</sub>H<sub>17</sub>IN<sub>6</sub>: C, 40.64; N, 21.87; H, 4.46; Found: C, 40.77; N, 21.80; H, 4.55.

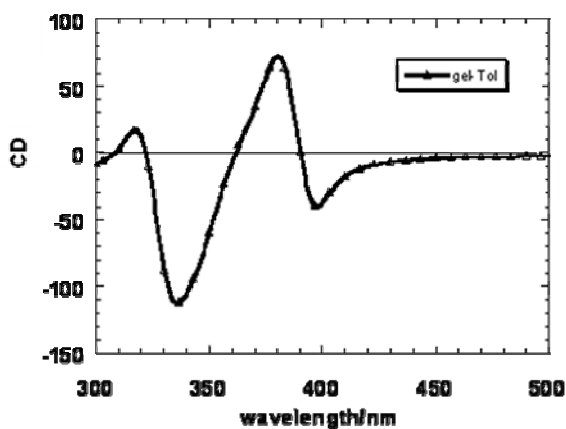
***N*<sup>2</sup>,*N*<sup>2'</sup>-(4,4'-(4,5-bis((*S*)-2-methylbutoxy)-1,2-phenylene)bis(ethyne-2,1-diyl)bis(4,1-phenylene))bis(*N*<sup>4</sup>-butyl-1,3,5-triazine-2,4,6-triamine)(**1**):** A schlenk tube containing 1,2-bis((*S*)-2-methylbutoxy)-4,5-diethynylbenzene (synthesized according to the literature,<sup>[2]</sup> 0.36 g, 1.2 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (70 mg, 0.06 mmol), *N*<sup>2</sup>-butyl-*N*<sup>4</sup>-(4-iodophenyl)-1,3,5-triazine-2,4,6-triamine(**4**) (1.6 g, 3 mmol) and CuI (14 mg, 0.06 mmol) was evacuated and back-filled with nitrogen for three times. Then degassed TEA (30 mL) was added to the tube under nitrogen atmosphere. The tube was sealed and the reaction mixture was stirred at room temperature for 48 hours. Then the solvent was removed in vacuo and the residue was purified by flash column chromatography over silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 20:1) to give the product as brown powder (0.42 g, 42%). <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO): δ 9.18 (s, 1H, -*NHAr*), 9.02 (s, 1H, -*NHAr*), 7.87 (d, *J* = 8.7 Hz, 4H, PhH), 7.35 (d, *J* = 8.7 Hz, 4H, PhH), 7.09 (s, 2H, PhH), 6.83 (br s, 2H, -*NHBu*), 6.42 (br s, 2H, -*NH*<sub>2</sub>), 6.26 (br s, 2H, -*NH*<sub>2</sub>), 3.90-3.78 (m, 4H, -*OCH*<sub>2</sub>*CH*-), 3.23 (q, *J* = 7.2 Hz, 4H, -*NHCH*<sub>2</sub>*CH*<sub>2</sub>-), 1.82 (m, 2H, -*OCH*<sub>2</sub>*CH*-), 1.66-1.21 (m, 12H, -*CH*<sub>2</sub>-), 0.95-0.88 (m, 12H, -*CH*<sub>3</sub>), <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>, 40°C): δ 166.5, 166.45, 164.6, 149.4, 139.5, 132.1, 119.7, 119.1, 117.5, 116.0, 92.4, 88.3, 74.1, 40.6, 34.8, 31.8, 26.2, 20.1, 16.5, 13.7, 11.3; ESI MS: 811.6 (M<sup>+</sup>); Anal. Calcd for C<sub>46</sub>H<sub>58</sub>N<sub>12</sub>O<sub>2</sub>: C, 68.12; N, 20.72; H, 7.21; Found: C, 68.05; N, 20.45; H, 7.23.

### III. Concentration and Temperature Dependent $^1\text{H}$ NMR Spectra



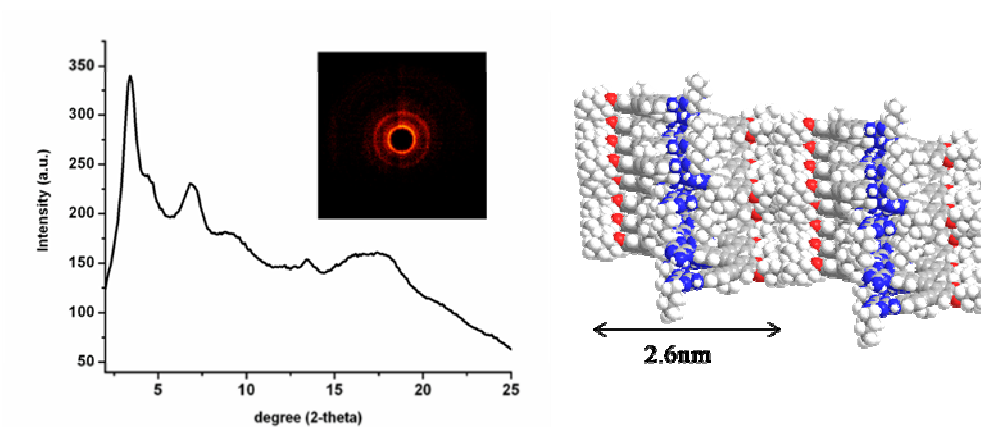
**Fig. S1.** (a):Molecular structure and  $^1\text{H}$  NMR assignments of molecule **1** in  $\text{CDCl}_3$  at  $50\text{ }^\circ\text{C}$ ; (b): Partial  $^1\text{H}$  NMR spectra at room temperature of molecule **1** in  $\text{CDCl}_3$  at the concentration of  $1.0 \times 10^{-2}\text{ M}$ ;  $8.0 \times 10^{-3}\text{ M}$ ;  $5.0 \times 10^{-3}\text{ M}$ ;  $3.6 \times 10^{-3}\text{ M}$ ;  $2.5 \times 10^{-3}\text{ M}$ ; (from top to bottom). The concentration-dependent  $^1\text{H}$  NMR spectra suggested aggregation occurred in the solution. (c): Variable-temperature  $^1\text{H}$  NMR spectra of molecule **1** in  $\text{CDCl}_3$  at  $30\text{ }^\circ\text{C}$ ,  $35\text{ }^\circ\text{C}$ ,  $40\text{ }^\circ\text{C}$ , and  $50\text{ }^\circ\text{C}$  (from top to bottom).

### IV. CD Spectra



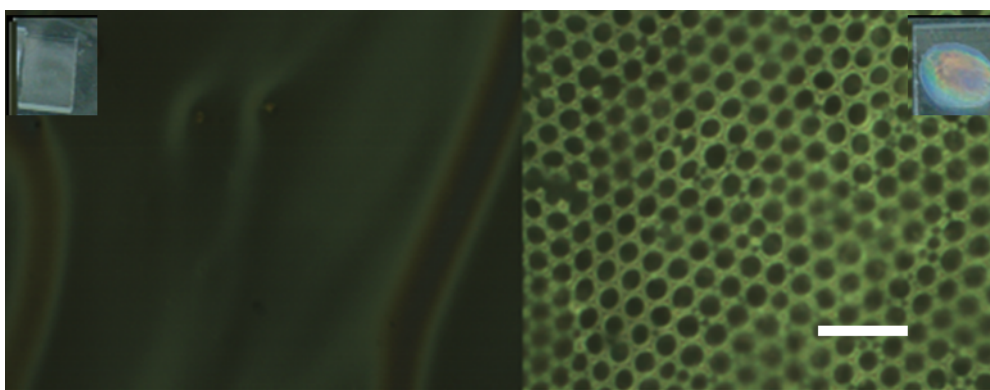
**Fig. S2.** CD spectra of gel in toluene.

## V. X-ray Diffraction Patterns



**Fig. S3.** X-ray diffraction patterns of xerogel of **1** in  $\text{CHCl}_3$  at room temperature.

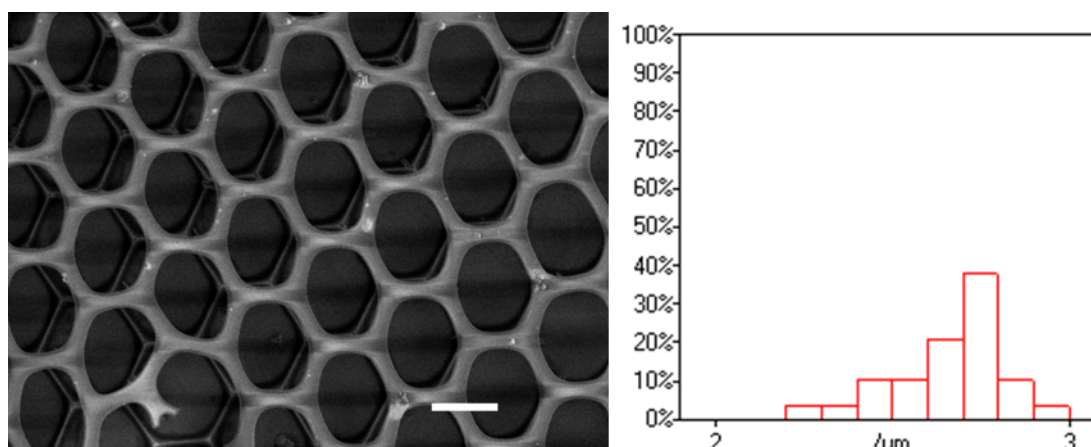
## VI. Optical Microscope Images



**Fig. S4.** Optical microscope images of the control film and honeycomb film fabricated by breath figure method.

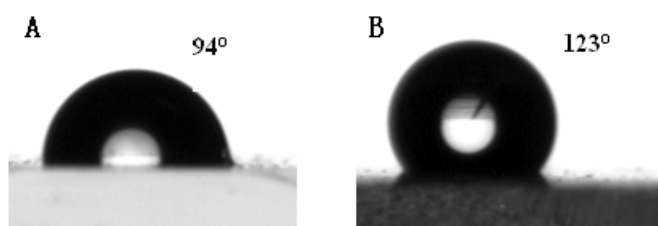
Scale bar is 10  $\mu\text{m}$ .

## VII. Distribution of the Pore Sizes of the Honeycomb Film



**Fig. S5.** Distribution of the pore sizes of the honeycomb film in Fig. 3a.

### VIII. Contact Angle Measurement



**Fig. S6.** Contact Angle of unpatterned film (A) and honeycomb film by BF method (B).

### IX. References

(1) Bielejewska, A. G.; Marjo, C. E.; Prins, L. J.; Timmerman, P.; de Jong, F.; Reinhoudt, D. N.

*J. Am. Chem. Soc.* **2001**, *123*, 7518-7533.

(2) Zhu, N.; Hu, W.; Han, S.; Wang, Q.; Zhao, D. *Org. Lett.*, **2008**, *10*, 4283-4286.