

## **Mechanism Insight into the Constitutional Phase Change Selection of Dynameric Frameworks Libraries**

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## 1. General methods

Reagents were obtained from Manchester organics (aldehyde **1**) and Sigma Aldrich (diamines **2-3**) and used as received.  $^1\text{H-NMR}$  spectra were recorded on an ARX 300 MHz Bruker. Chemical shifts are reported as  $\delta$  values (ppm) with  $\text{CDCl}_3$  ( $^1\text{H-NMR}$   $\delta$  7.26) or  $\text{CD}_3\text{CN}$  ( $^1\text{H-NMR}$   $\delta$  1.94) as an internal standard. Contact angle were analyzed by homemade device, equipped with Olympus camera (OM-system,  $f = 50$  mm), and 4.4 W light (Figure S1). SEM images and EDX were obtained with a Hitachi S-4500 apparatus, under a tension of 0.5-30 kV. Water transport property was tested by Sterlitech HP4750 stirred cell, with active membrane area of  $14.6\text{ cm}^2$ , maximum processing volume of 300 mL and cell height of 22.4 cm (Figure S2).

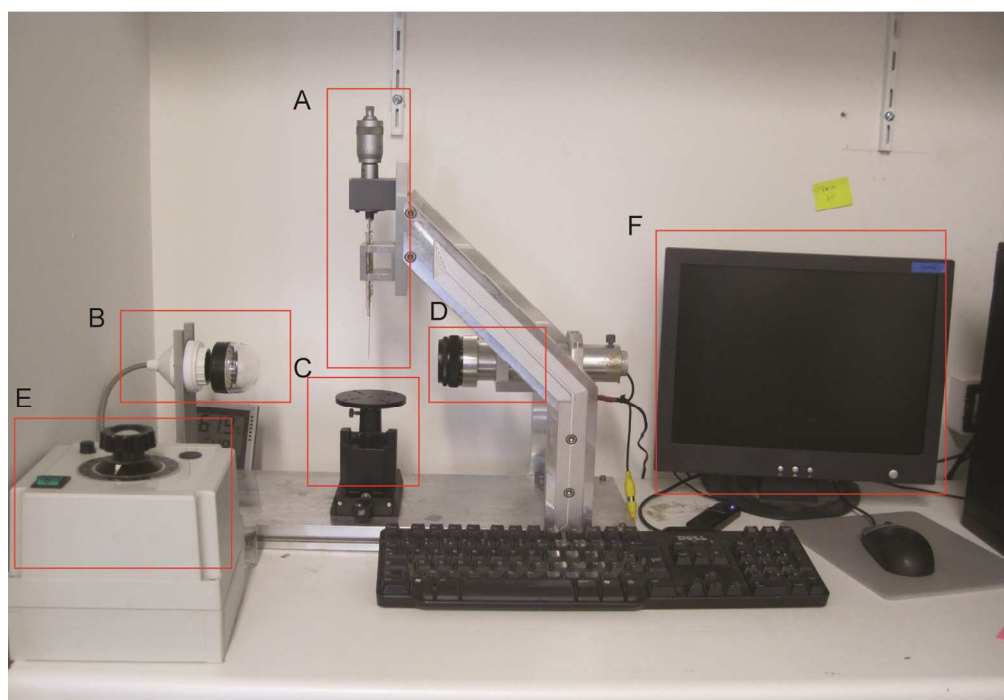


Figure S1. Homemade device for contact angle measurement: A) needle and volumn control of water droplet; B) light; C) membrane support; D) camera; E) light control; F) computer.

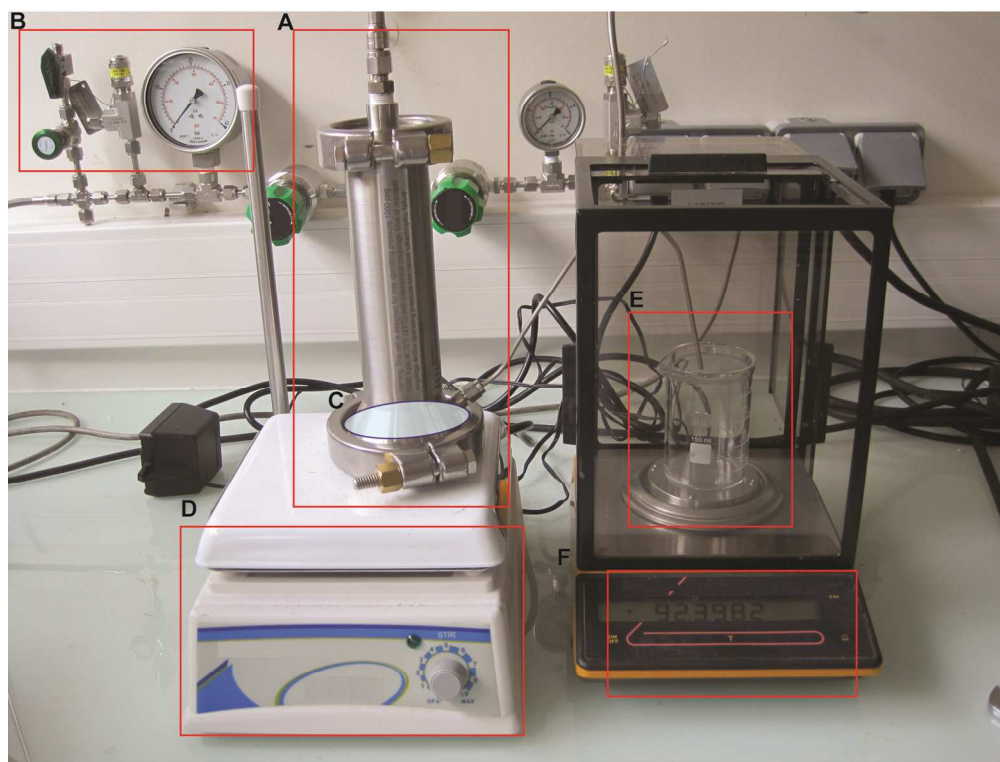
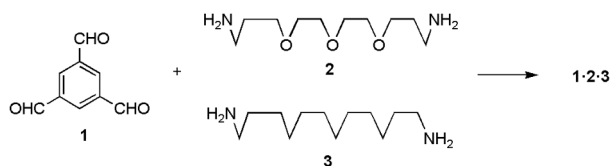


Figure S2. Homemade device for water transport measurement: A) Sterlitech HP4750 stirred cell; B) pressure control; C) schematic showing membrane position; D) magnetic stirrer; E) water output and collection; F) balance to measure water mass.

## 2. Typical synthesis

Benzene-1,3,5-tricarbaldehyde and corresponding diamines were added in a flask together with 15 mL  $\text{CH}_3\text{CN}$  or  $\text{CHCl}_3$  (Table S1). The reaction mixture was stirred at  $60^\circ\text{C}$  for 10 min (stopped when the reaction starting get unclear). Then the solution was cooled down to r.t. and poured into a Teflon or glass mold through a filter paper, and was subsequently exposed to slow evaporation inside the hood at r.t. The solid membrane can be formed within 3 h.

Table S1. Synthesis of **1·2·3**



chemicals	Mw (g/mol)	n (mmol)	eq.	m (mg)
<b>1</b>	162.14	0.9	1.0	145.8
<b>2</b>	148.20	0.6	0.75	148.8
<b>3</b>	144.26	0.6	0.75	135.3

### 3.NMR spectra

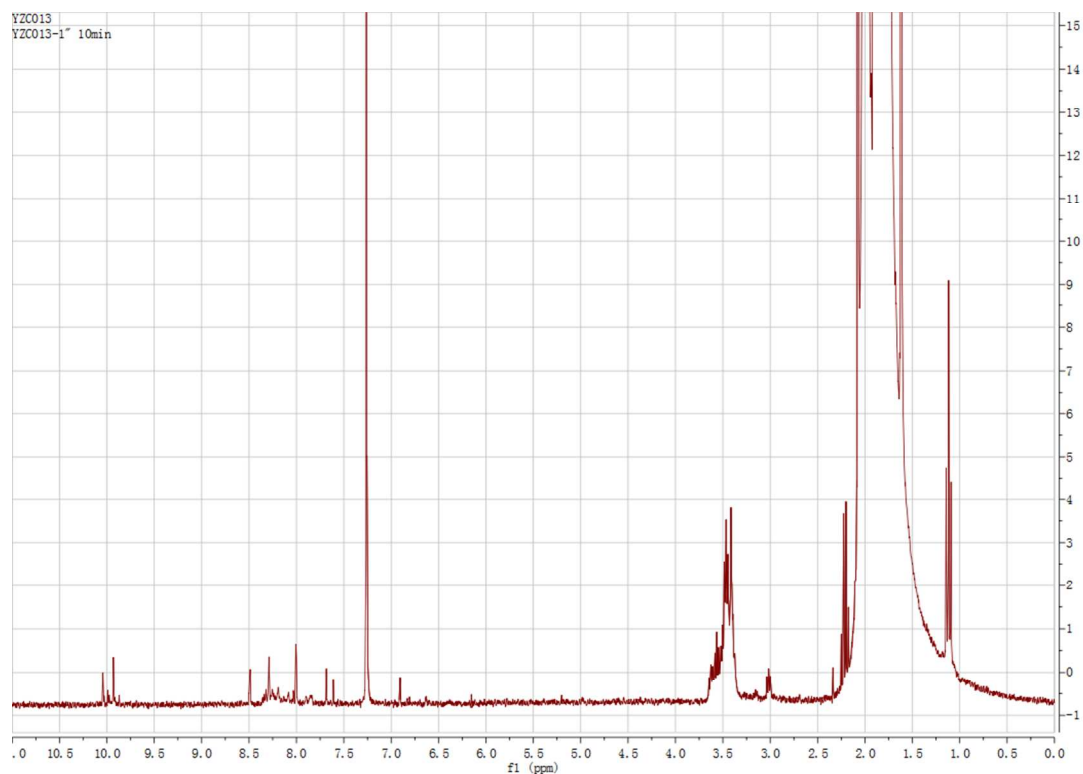


Figure S3.  $^1\text{H}$ -NMR spectrum of  $1\cdot 2\cdot 3$  in  $\text{CHCl}_3$ .

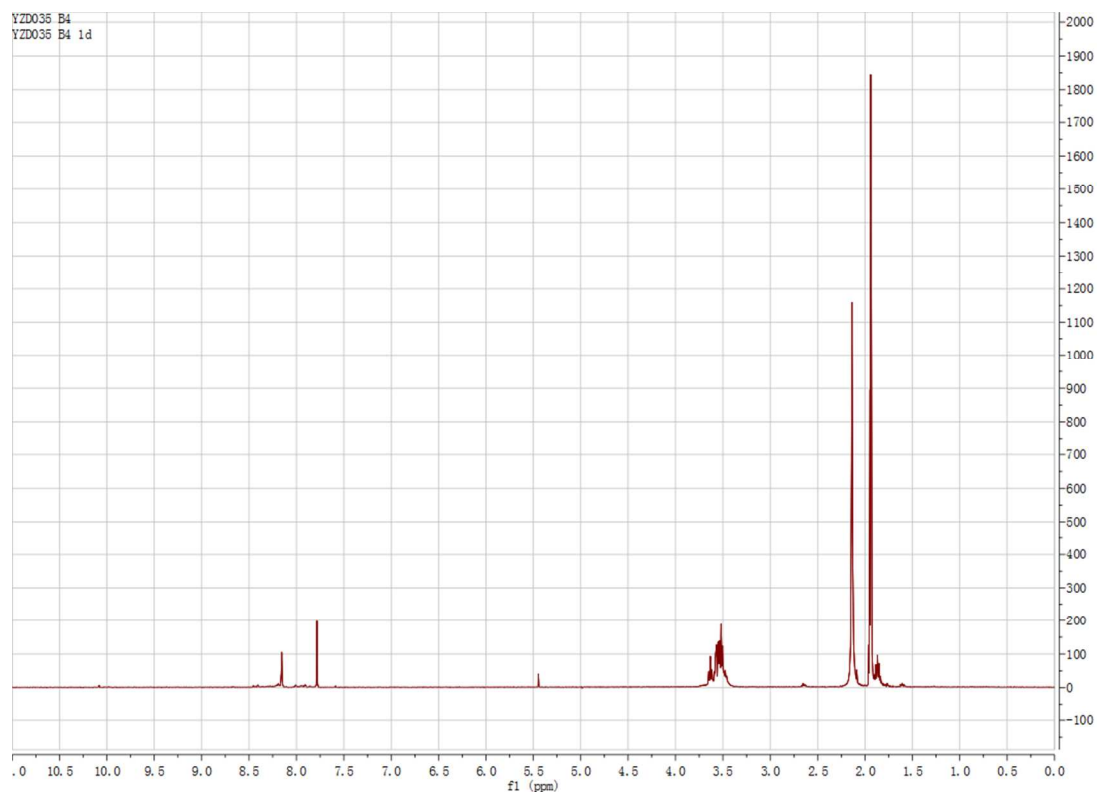


Figure S4.  $^1\text{H}$ -NMR spectrum of  $1\cdot 2$  (1:1.5 ratio) in  $\text{CH}_3\text{CN}$  after 1 day.

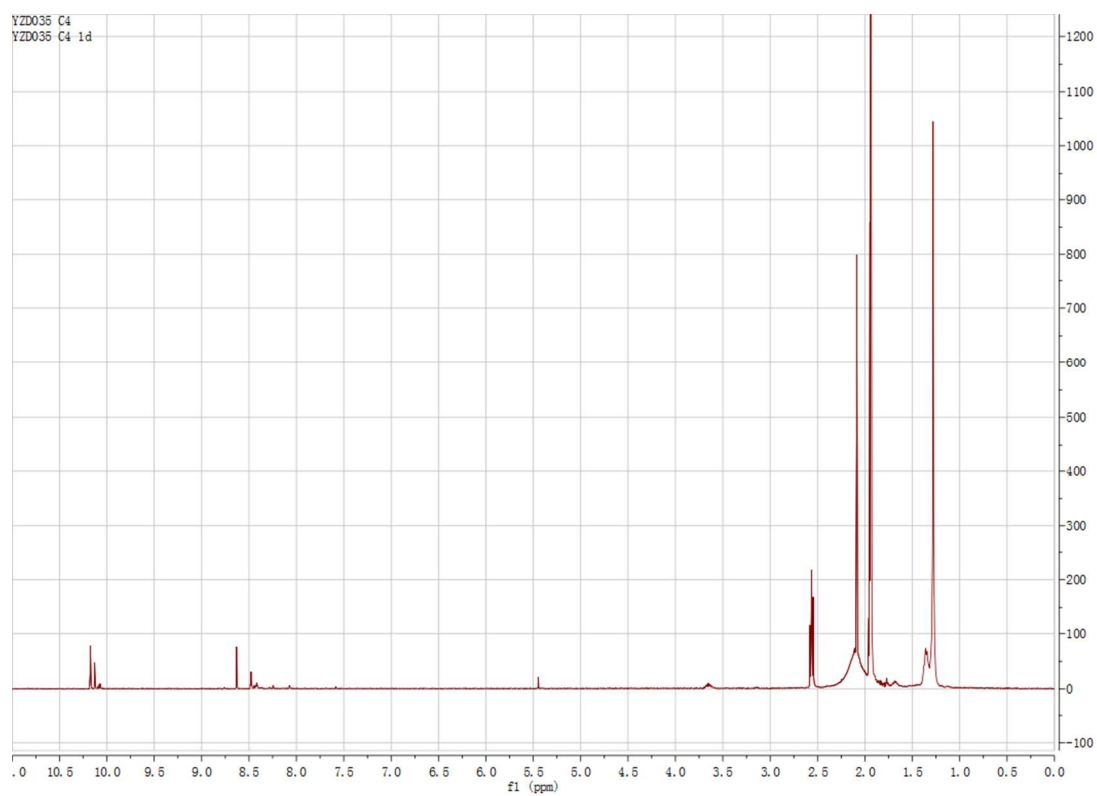


Figure S5.  $^1\text{H}$ -NMR spectrum of **1·3** (1:1.5 ratio) in  $\text{CH}_3\text{CN}$  after 1 day.

#### 4. FTIR spectra of the membranes

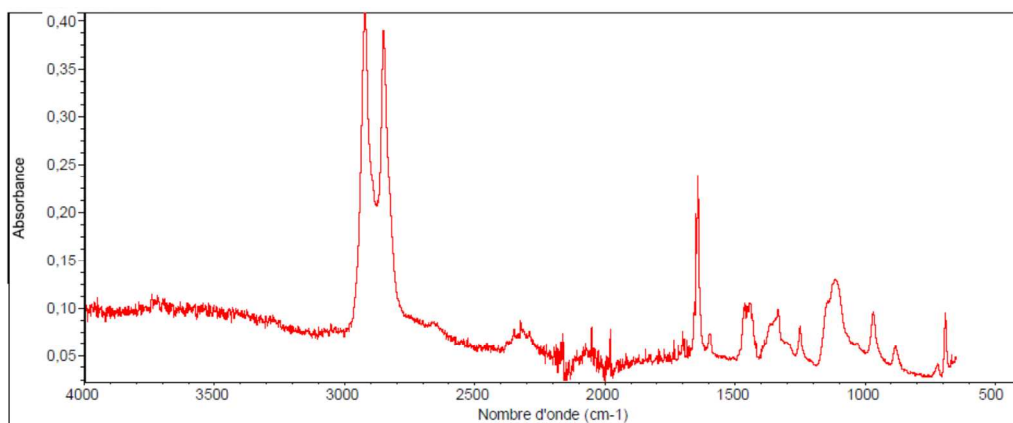


Figure S6. Typical FTIR spectrum of **1·2·3** (1:1.5 ratio) made from CH<sub>3</sub>CN.

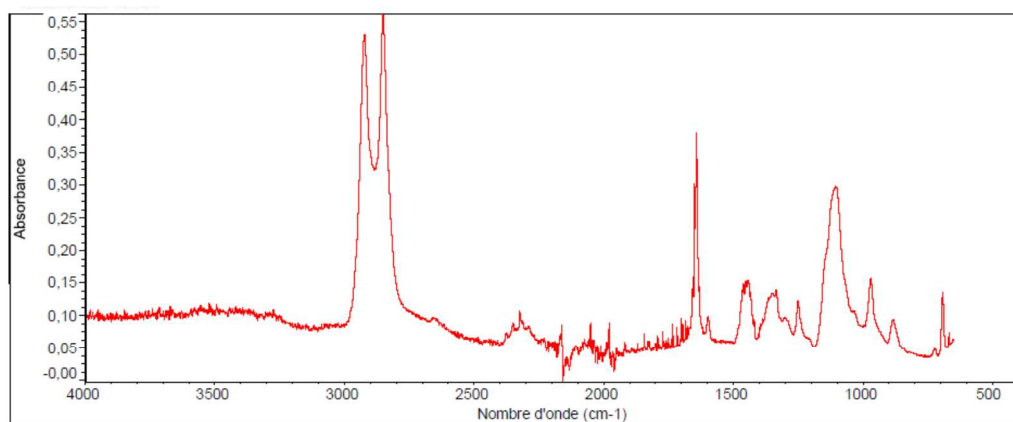


Figure S7. Typical FTIR spectrum of **1·2·3** (1:1.5 ratio) made from CHCl<sub>3</sub>.

## 5. Scanning electron microscope (SEM) images

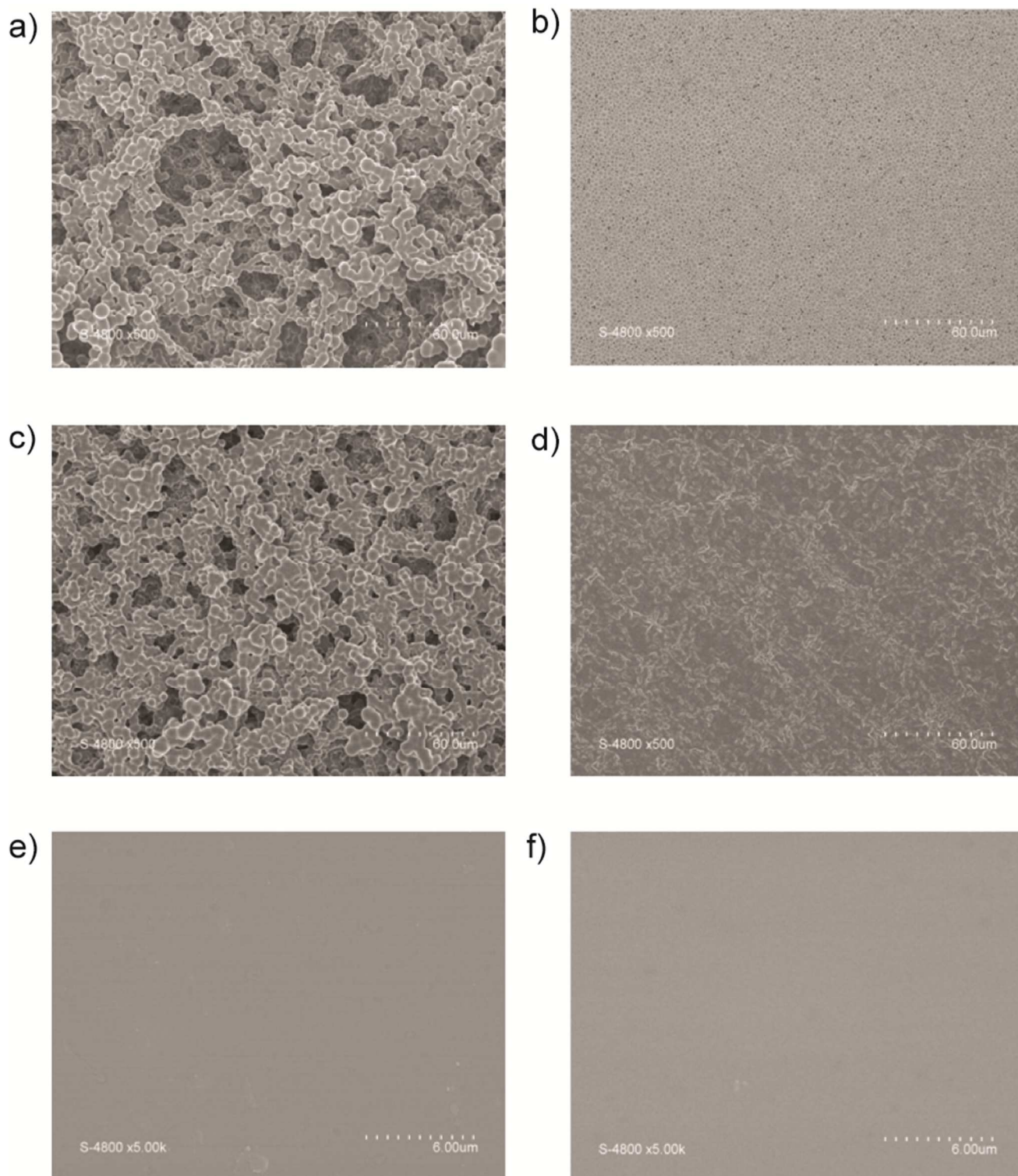


Figure S8. SEM images of **1·2·3** with a-b) Teflon template in  $\text{CH}_3\text{CN}$ ; c-d) glass template in  $\text{CH}_3\text{CN}$  and e-f) Teflon template in  $\text{CHCl}_3$ . The left column is the top side and the right column is the bottom side of the membranes.



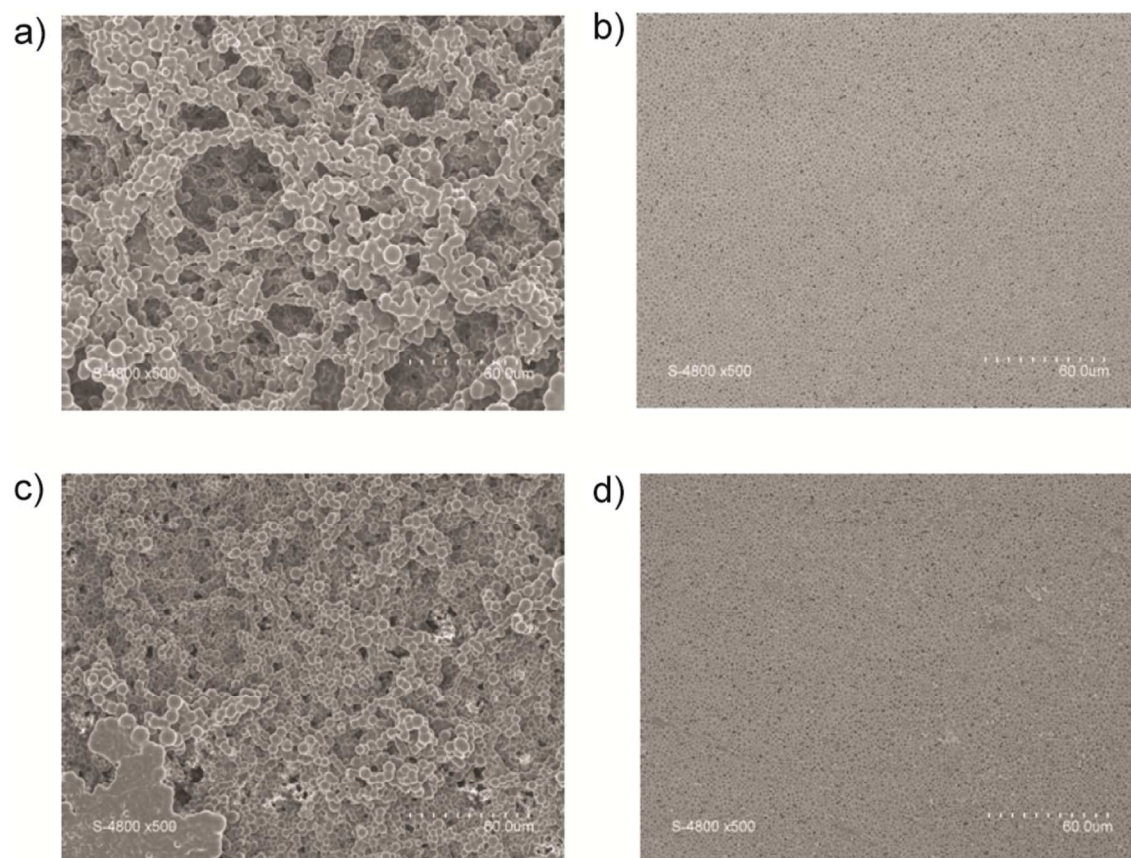
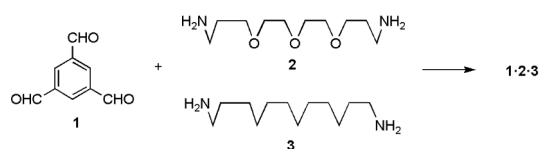


Figure S9. SEM images of **1·2·3** with stability test in water: a-b) original membrane; c-d) 1 week in water with the same membrane. The left column is the top side and the right column is the bottom side of the membranes.

## 6. Contact angle (CA) analyses of the membranes containing different 2:3 ratios



ratio <b>2:3</b>	Top side	Bottom side
2:1	65.4	57.6
2:3	87.7	80.6
3:2	65.3	91.8
1:2	56.8	84.6



## 7 Dynamic light scattering (DLC) measurements

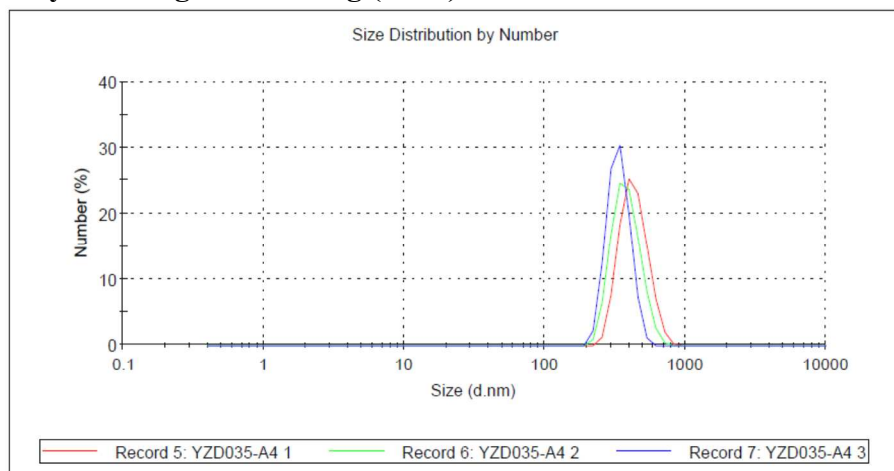


Figure S10. DLS results for dynamer solution 1·2·3(ratio 1 : 2 : 3 = 1 : 0.75 : 0.75).

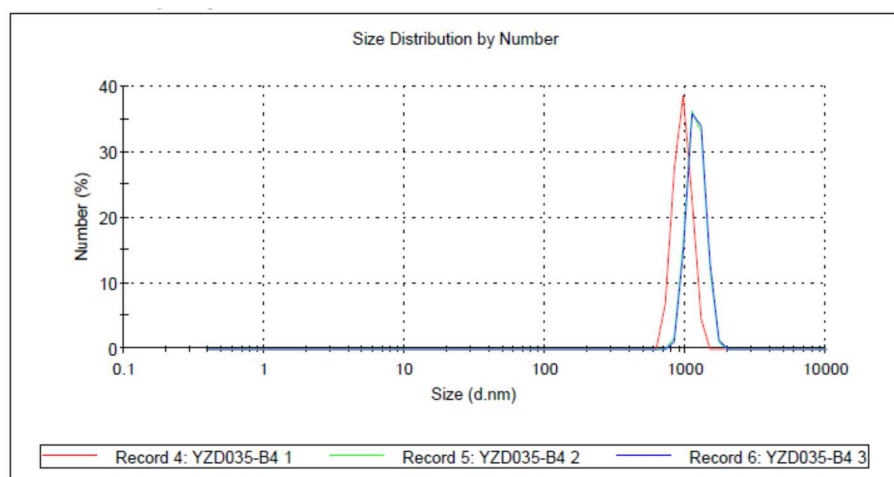
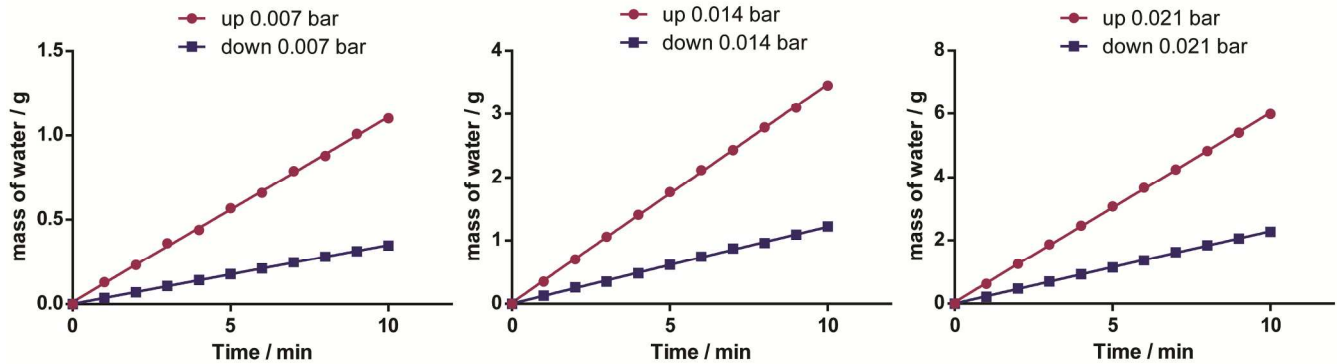


Figure S11. DLS results for dynamer solution 1·2 (ratio 1 : 2 = 1 : 1.5).

## 8. Water transport tests

Ratio **2** to **3** = 2:1



Ratio **2** to **3** = 1:2

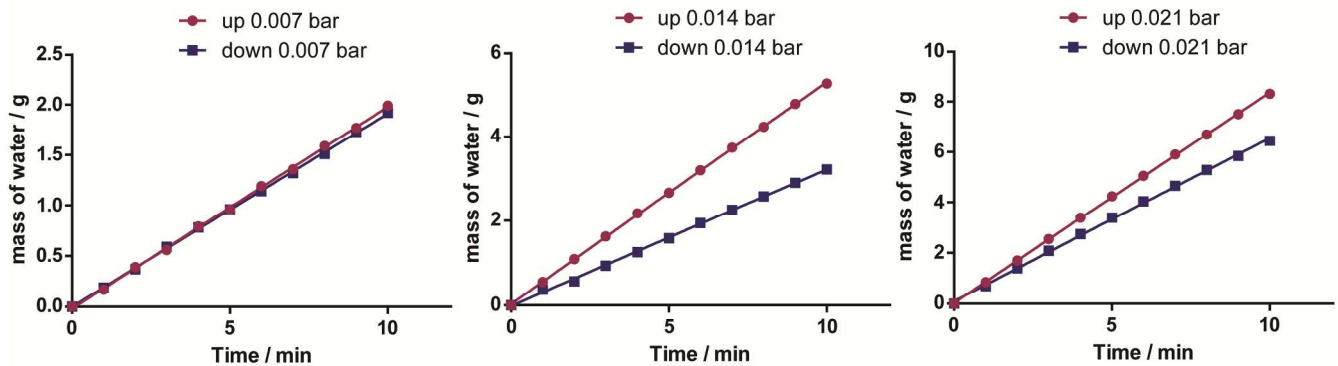


Figure S12. Water transport graphs of **1·2·3** with different 2:3 ratios under different pressures.

## 9. Water permeability calculation

Water permeability is calculated from the slop of the line mass flux verses pressure (Figure S9), the mass flux was calculated from the slop of mass verses time (Figure S8), then divided by the active membrane area of  $14.6 \text{ cm}^2$ .

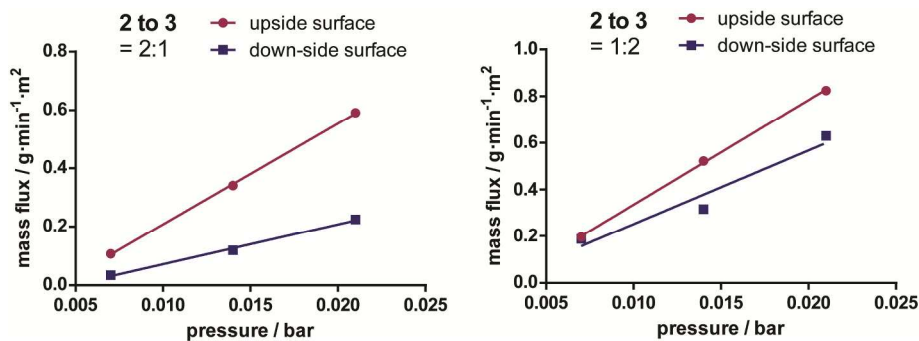


Figure S13. Water permeability (the slop) calculation of **1·2·3** with different **2:3** ratios.