Supporting Information

Covalent organic framework modulated interfacial polymerization for ultrathin desalination membranes

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2. Experimental section

2.1 Preparation of covalent organic framework[1]

0.3 mmol of 1,3,5-triformylphloroglucinol (Tp), 0.45 mmol of p-phenylenediamine (Pa-1), 1.5 mL of mesitylene, 1.5 mL of 1,4-dioxane and 0.5 mL of 6 M aqueous acetic acid were added into a Pyrex tube (o.d. × i.d. = 5 × 4 mm^2 and length 10 cm). Then the mixture was sonicated for 10 minutes to ensure homogeneous dispersion. The tube was flash frozen at 77 K (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles. After sealing off, the tube was then heated at 120 °C for 72 h. A red colored precipitate was collected by centrifugation and washed it successively by acetone, tetrahydrofuran and dichloromethane. The powder collected was then solvent exchanged with acetone 2-3 times and stirred for 48 h. Finally, the powder was dried at 120 °C under vacuum for 12 h to get a deep red colored powder in ~80% isolated yield.

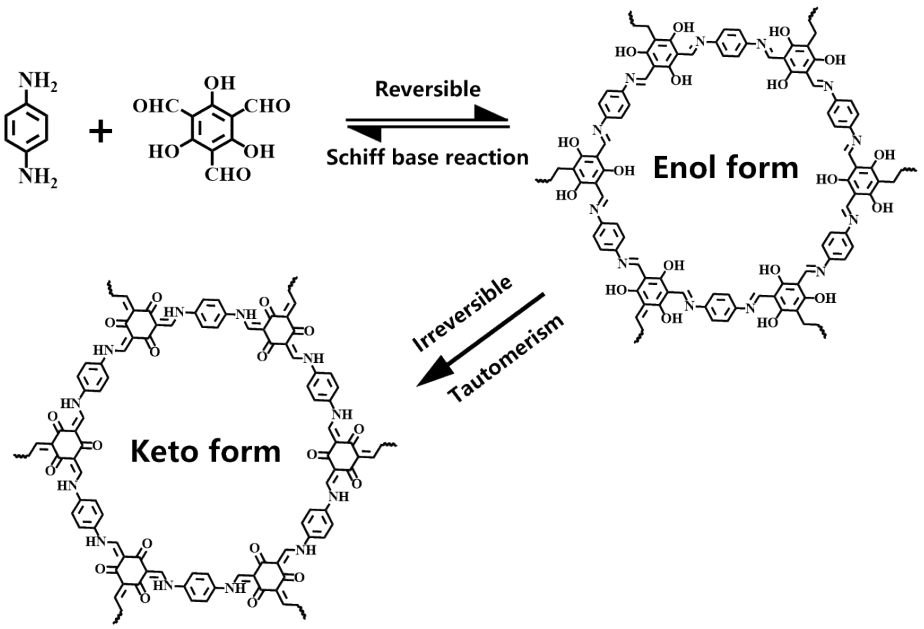

Fig. S1. Schematic representation of the synthesis of TpPa-1by the combined reversible and irreversible reaction of 1,3,5-triformylphloroglucinol with p-phenylenediamine.

2.2 Preparation of covalent organic framework nanosheets[2]

80 mg of as-prepared covalent organic framework was placed in a mortar (i.d.= 100 mm) and grounded with 1-2 drops of methanol for 1 h. The fine powders were then dispersed in 100 mL of methanol. The resulting suspension was centrifuged at 8000 rpm for 5 min to obtain a clear solution. After the complete evaporation of methanol,

the resultant TpPa-1 covalent organic framework nanosheets (CONs) were obtained.

Table S1. Mass density of CONs for different CLS substrate.

Samples	content of CONs loading(mg)	Mass density (g/m^2)
CLS(1)	0.1	0.058
CLS(2)	0.2	0.116
CLS(3)	0.3	0.173
CLS(4)	0.4	0.231
CLS(5)	0.5	0.289
CLS(6)	0.6	0.347

Table S1 listed the mass density of CONs for different CLS substrate. For convenient narration, the fabricated substrates were designed as CLS(x) where x represented the content of CONs loading. For example, CLS(5) was the substrate with CONs loading of 0.5 mg.

3. Results and discussion section

3.1 Characterization of CONs

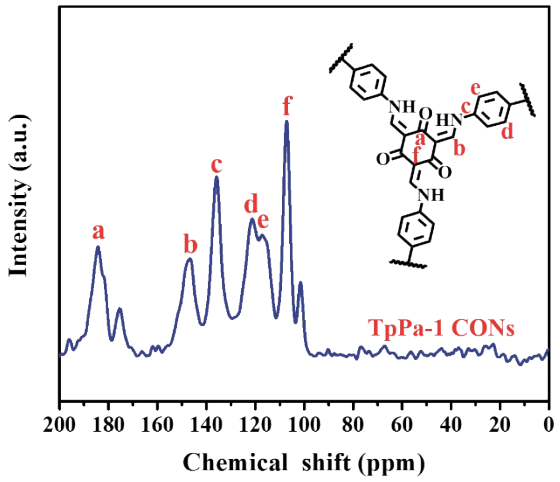

Fig. S2 The ^{13}C CP-MAS solid-state NMR spectra of CONs.

As shown in Fig. S2, the TpPa-1 CONs showed characteristic peaks at 184 ppm for carbonyl carbons (-C=O) and 107 ppm for exocyclic carbons (-C=C), in accordance with previous reports1,2. The disappearance of peak at 190 ppm (corresponding to -CHO) gave clear evidence for the complete consumption of the 1,3,5-

triformylphloroglucinol starting monomer.

3.2 Characterization of PA/CLS membranes

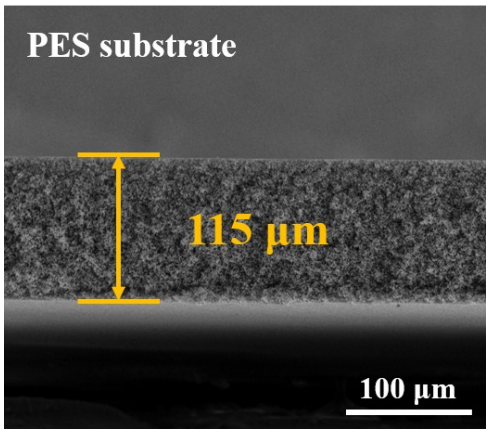

Fig. S3 Cross sectional SEM image of PES substrate.

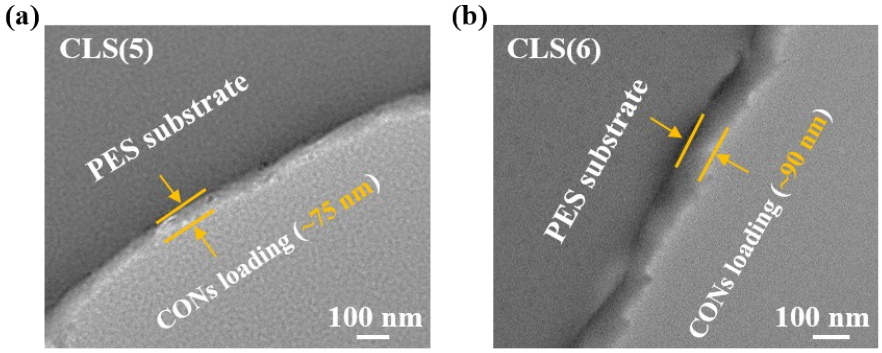

Fig. S4. Cross sectional TEM image of CLS(5) and CLS(6).

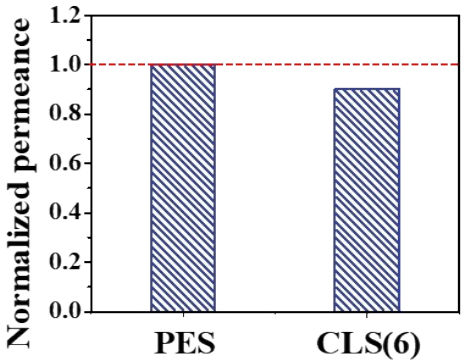

Fig. S5. Normalized permeance of PES and CLS(6) substrate.

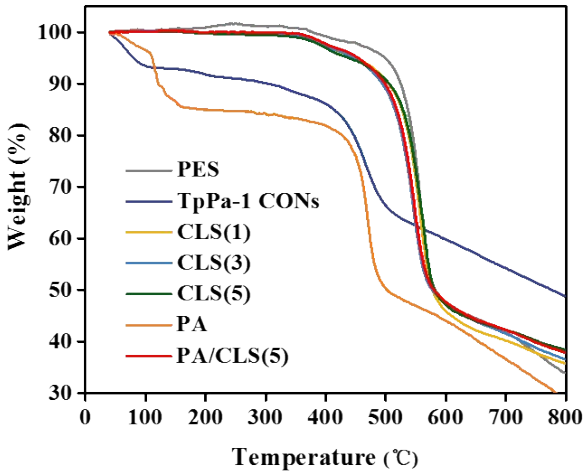

Fig. S6. (a) TGA curves of PES, TpPa-1 CONs, CLS(1), CLS(3), CLS(5), PA and PA/CLS(5).

Fig. S7. The digital photographs of membranes with different loading content of CONs.

Table S2. Surface compositions of PA/CLS(X) membranes from XPS data (in atomic percent).

Membrane	O (%)	N (%)	O/N	D (%)[a]
PA/PES	17.79	9.91	1.79	10.01
PA/CLS(1)	15.22	10.25	1.48	41.45
PA/CLS(3)	14.66	10.86	1.35	55.36
PA/CLS(5)	17.09	13.01	1.31	59.74

[a] The crosslinking degree (%) was calculated based on the O/N ratio.

Table S2 summarized the elementary composition of as-prepared PA skin layer modulated by different substrate with varied content of CONs loading.

The crosslinking degree(D) was calculated as follows:

$$\frac{O}{N} = \frac{3m+4n}{3m+2n}$$

$$D = \frac{m}{m+n} \times 100\%$$

where m and n were the cross-linked and linear proportion of the PA selective layer, respectively.

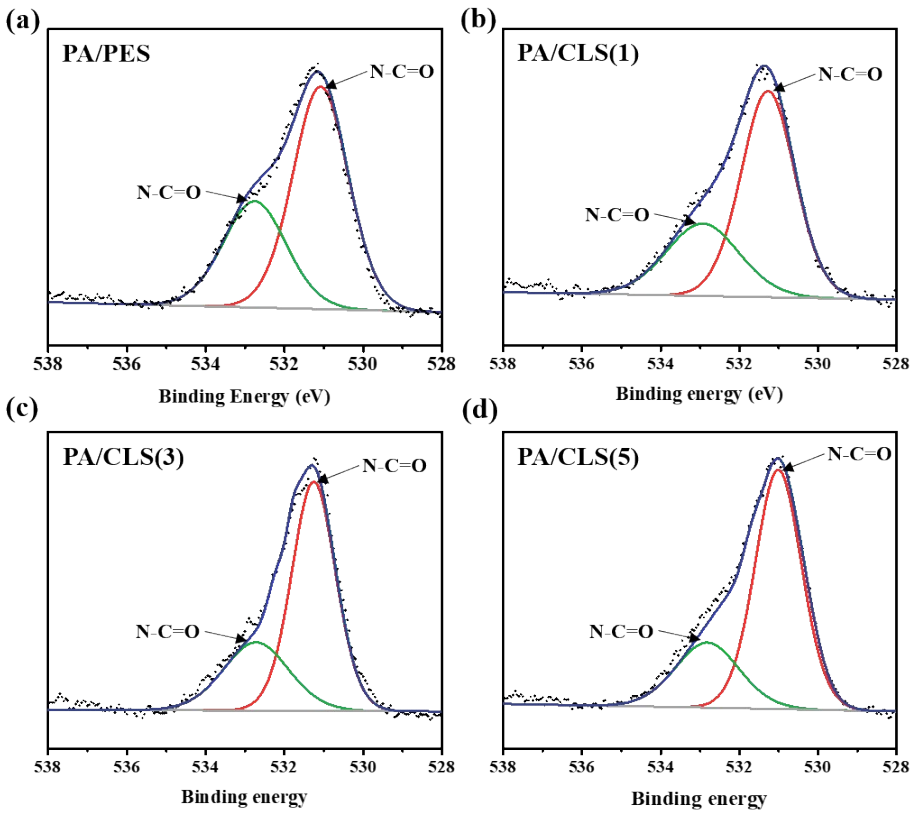

Fig. S8. High-resolution XPS spectra of PA/PES, PA/CLS(1), PA/CLS(3) and PA/CLS(5) membranes. Convoluted high-resolution O1s (a-d).

Table S3. Species and composition determined from the deconvolution of O1s core level XPS spectra calculated based on Fig. S3.

Membrane	N-C=O	O-C=O
PA/PES	64.87	35.13
PA/CLS(1)	67.76	32.24
PA/CLS(3)	69.36	30.66
PA/CLS(5)	72.78	27.22

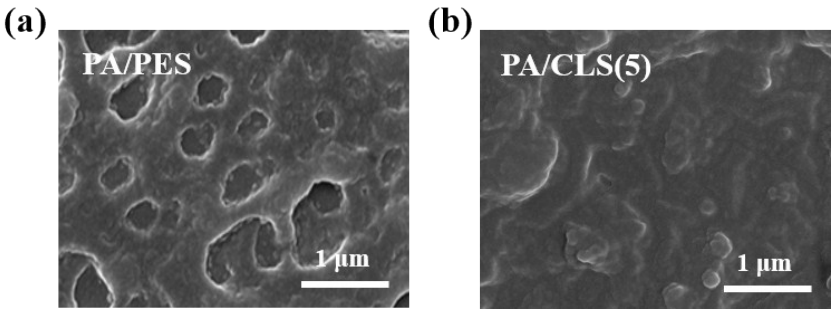

Fig. S9. SEM images of PA/PES and PA/CLS(5) membrane.

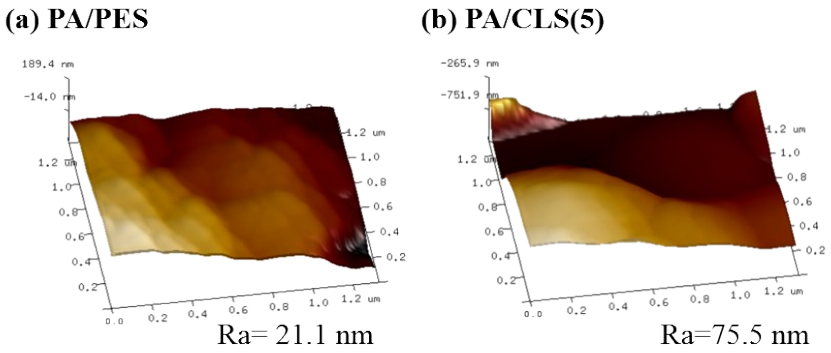

Fig. S10. AFM images and surface roughness (Ra) of PA/PES and PA/CLS(5) membrane.

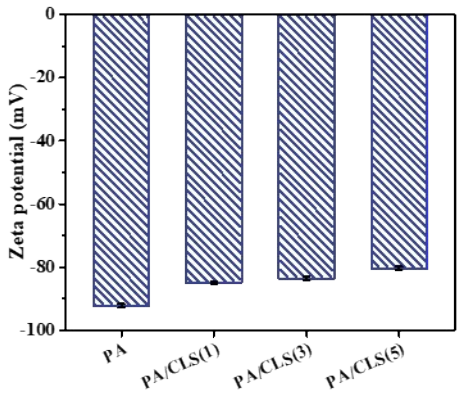

Fig. S11. Chargeability of PA/PES, PA/CLS(1), PA/CLS(3) and PA/CLS(5) membranes.

The zeta potential was measured utilizing 0.001 mol/L KCl solution (pH=6.0±0.2) at 25±0.5 °C and each sample was measured for 4 times to eliminate error. Each above value was based on the average of two independent membranes fabricated under the same condition.

3.3 Separation performance of PA/CONs membrane

Table S4. The summary of separation performance of all the membranes tested in this work.

Membrane name	Pure water flux ($L\ m^{-2}\ h^{-1}$)	Permeance ($L\ m^{-2}\ h^{-1}\ MPa$)	Na_2SO_4 rejection (%)
PA/PES	31.3	156.6	85.9
PA/CLS(1)	41.6	207.9	93.1
PA/CLS(2)	64.4	321.8	92.7
PA/CLS(3)	74.1	370.2	93.0
PA/CLS(4)	82.6	413.0	93.9
PA/CLS(5)	107.1	535.5	94.3
PA/CLS(6)	97.5	487.4	93.7

Table S4 summarized the pure water flux and salt rejection of all the membranes tested in this work. (Testing condition: 1000 ppm salt feed under 0.2 MPa; 25 °C; 0.9 cm^2 membrane area; each above value was based on the average of two independent membranes fabricated under the same condition)

Table S5. Comparison of the separation performance of different membranes in the literatures.

	Membrane	Flux ($L\ m^{-2}\ h^{-1}\ MPa^{-1}$)	Na_2SO_4 Rejection (%)	Reference
Membranes prepared by new monomers	Polycyclenamide NF	40.3	94.1	[3]
	DCH-TMC NF	74.3	98.1	[4]
	TFC NF-PO	268.3	92.1	[5]
	PA@DCA	21.6	98.0	[6]
	NFM-4	71.8	97	[7]
Membranes fabricated with nanomaterials	Si/PIP-amide TFC NF	78.0	97.4	[8]
	PEG-POSS-PA	163.5	87.1	[9]
	PA/TNT	74.8	96.4	[10]
	GO/TFN	156.3	96.6	[11]
	TFN(DOX)	201.0	90.0	[12]
Membranes formed on optimized substrate	PA/PD/SWCNTs	320.0	95.9	[13]
	PA/CNC/PES	340.0	97.0	[14]

	PA/PDA/PEI	98.0	96.8	[15]
	UCN	327.0	70.8	[16]
	TFC NFMs	175.7	95.0	[17]
Commercial membranes	NF270(DOW)	148.0	98.0	[18]

References

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