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## **Supplementary Information**

## **Tailored Preparation of Porous Aromatic Frameworks in Confined**

## Environment

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## Supplementary characterization



**Fig. S1** SEM image of PS/PAF-1 hybrid membrane formed on silicon substrates prior to membrane transfer.

In order to verify that PAF-1 powder was successfully obtained, the structure and composition of PAF-1 powder have been characterized by FT–IR spectroscopy and solid–state <sup>13</sup>C CP/MAS NMR spectroscopy. As shown in **Fig. S2a**, the disappearance of the C–Br bonds (~1078 cm<sup>-1</sup>, 500-600 cm<sup>-1</sup>) indicates the complete conversion of TBMP. The resonance signals at 146, 140, 131, 125, and 64 ppm are resolved (**Fig. S2b**), which are consistent with the previous report.<sup>5</sup> In addition, the nitrogen adsorption-desorption isotherm of PAF-1 powder was tested at 77 K which shows a classic type I isotherm according to **Fig. S2c**. The Brunauer–Emmett–Teller (BET) surface area of PAF-1 was calculated to be 4765 m<sup>2</sup>/g. The pore size of PAF-1 was calculated to be 1.19 nm (**Fig. S2d**).



**Fig. S2** a) FT–IR spectra of the TBMP (grey) and PAF-1 powder (red) from 400-1600 cm<sup>-1</sup>; b) Solid–state <sup>13</sup>C CP/MAS NMR spectrum of PAF-1; c) Nitrogen adsorption-desorption isotherm measured at 77 k for PAF-1; d) The pore size of PAF-1 was calculated according to Density Functional Theory (DFT).



Fig. S3 FT–IR spectrum of poly(4-bromostyrene-co-styrene) brushes.



Fig. S4 FT–IR spectra of the TBB (blue) and PAF-5 powder (orange) from 400-1600 cm<sup>-1</sup>.

![](_page_4_Figure_0.jpeg)

**Fig. S5** AFM scans and the corresponding of section view of PS/PAF-1 hybrid membrane before a) and after b) the process of membrane transfer.

![](_page_4_Figure_2.jpeg)

Fig. S6 HRTEM images of on the regions of a) PS and b) PAF-1 of the hybrid membrane.

![](_page_5_Picture_0.jpeg)

Fig. S7 Continuous flow device.

![](_page_5_Figure_2.jpeg)

Fig. S8 Adsorption curve of PS/PAF-1 hybrid membrane.