Electronic Supporting Information

Organosiloxane membranes for heavy aromatic oil fractionation

Liang Ma,* Min Hou, Yuemei Wang, Weiyi Tong, Junlin Zheng

State Key Laboratory of Green Chemical Engineering and Industrial Catalysis, SINOPEC

Shanghai Research Institute of Petrochemical Technology Co.,Ltd., Shanghai 201208, China.

Email: maliangbuct@126.com

1. Experimental sections

1.1 Materials

Hexamethylenimine (99%, Sigma-Aldrich), hexadecyltrimethylammonium bromide (99.9%, Sigma-Aldrich), sodium hydroxide (98%, Sigma-Aldrich), sodium aluminate (technical grade, Shanghai Hushi Laboratorial Equipment Co., Ltd.), dichloromethane (technical grade, Shanghai Hushi Laboratorial Equipment Co., Ltd.), fume silica (Cab-o-Sil, M-5, scintillation grade, Cabot Corporation), hydroxyterminated polydimethylsiloxane (99%, average molecular weight of 50,000, Shandong Dayi Chemical Co., Ltd, China), 3-acryloxypropyl trimethoxysilane (98%, Macklin biochemical Co., Ltd.), dibutyltin dilaurate (97%, Macklin biochemical Co., Ltd.), 2-hydroxy-2-methylpropiophenone (97%, Macklin biochemical Co., Ltd.). These reagents were used as mentioned without further purification. Heavy aromatic oil was obtained from Sinopec Shanghai Petrochemical co., LTD. The deionized water was made in laboratory. The polyacrylonitrile (PAN) membrane with average pore size of 20 nm was purchased from Shandong MegaVision Membrane Techenology & Energineering Co. Ltd., China.

1.2 Synthesis of MCM-22 nanosheets

The MCM-22 nanosheets were synthesized on the basis of a previous report method with minor modification.[1] A mixture of sodium aluminate (0.06 g), 1.10 g cetyltrimethylammonium bromide (CTAB), hexamethylenimine (0.74 g), and 1.0 M sodium hydroxide solution (2.40 g) were dissolved in deionized water (9.50 g) and stirred for 12h at room temperature. Then, 0.92 g of fume silica was added and heated at 150 °C for a week with rotation (35 rpm). The as-synthesized product was collected by vacuum filtration, washed with deionized water for three times, and dried at 70 °C in the oven. Finally, the powders were calcined in the furnace at 550 °C for 12 h.

1.3 Preparation of organosiloxane membranes

Acrylate-functionalized organosiloxane was synthesized according to our previous study.[2] MCM-22 nanosheets were dispersed in dichloromethane and sonicated for 20 min. Then, organosiloxane was added to it and the mixture was stirred at 700 rpm for 2h at room temperature. The MCM-22 loading is calculated as the weight percentage of MCM-22 to the mixture of MCM-22 and organosiloxane. Then, the solution was casted on the polyacrylonitrile (PAN) substrate. The membranes were cured by under a UV lamp (365 nm).

1.4 Characterization

Field emission scanning electron microscope (FE-SEM, ZEISS Merlin) was used to characterize morphology of the composite membranes and zeolites samples. The samples were sputtered with 10 nm thick Pt coating under an argon atmosphere (2×10^{-2} mbar). X-ray photoelectron spectroscopy (XPS) was performed in a Kratos AXIS Ultra DLD spectrometer equipped with a monochromatic Al Kα X-ray source. Fourier transform infrared spectroscopy in the attenuated total reflectance (FTIR-ATR) mode was conducted by using a ThermoFisher Scientific Nicolet iS50 spectrometer. Transmission electron microscope (TEM, ThermoFisher Scientific Tecnai 20 S-TWIN) was used to perform the morphology of zeolite nanosheets. X-ray diffraction patterns studies were measured by X-ray powder diffractometer (D8 Advances SS, Brüker). Nitrogen physisorption (TriStar3000 3Flex, Micromeritics) performed to determine the porosity of zeolites samples. The analysis was conducted at 77 K. Thermogravimetric analysis (TGA) measurements (STA449F3-QMS403/SDT650/DSC2000, NETZSCH) at a rate of 10 °C min^{-1} heated from 25 to 900 °C under a nitrogen atmosphere. Water contact angles were tested by a contact angle measuring device (JC2000D3, Shanghai Zhongchen Corporation, China). The feed, permeate and retentate samples were analyzed using two-dimensional gas chromatography (GCxGC) system consisted of an Agilent 7890 gas chromatography (Agilent Technologies).

1.5 Organic solvent nanofiltration experiments

Liquid aromatic feedstocks separation experiments were carried out under 3.0 MPa at room temperature with flow rate of 1.0 L min^{-1}. The active area of membranes was 25.12 cm^2. The permeance was calculated by the following equation.

$$Permeance = \frac{V}{A \times \Delta t \times \Delta P}$$

Where V is the volume of permeated solution (L), Δt represents permeating duration (hour), A is the active area of the membrane (m^2), ΔP is the pressure (bar) . The unit of the permeance was liters per square meter per hour per bar (L m^{-2} h^{-1} bar^{-1}). The rejection (R) was determined as following:

$$R = \left(1 - \frac{c_p}{c_f}\right) \times 100\%$$

Where c_p is the concentration of permeate and c_f is the concentration of feed.
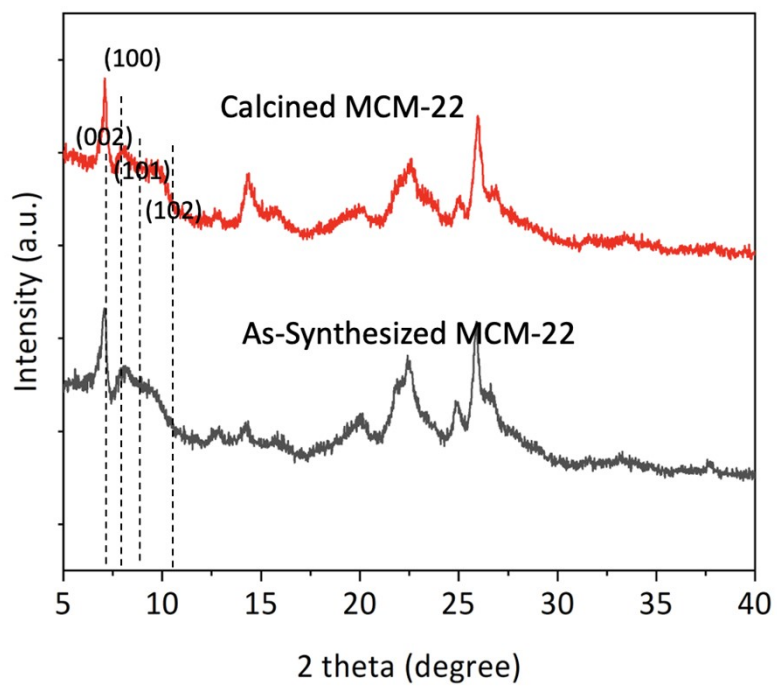
1.4 Supplementary Figures and Tables

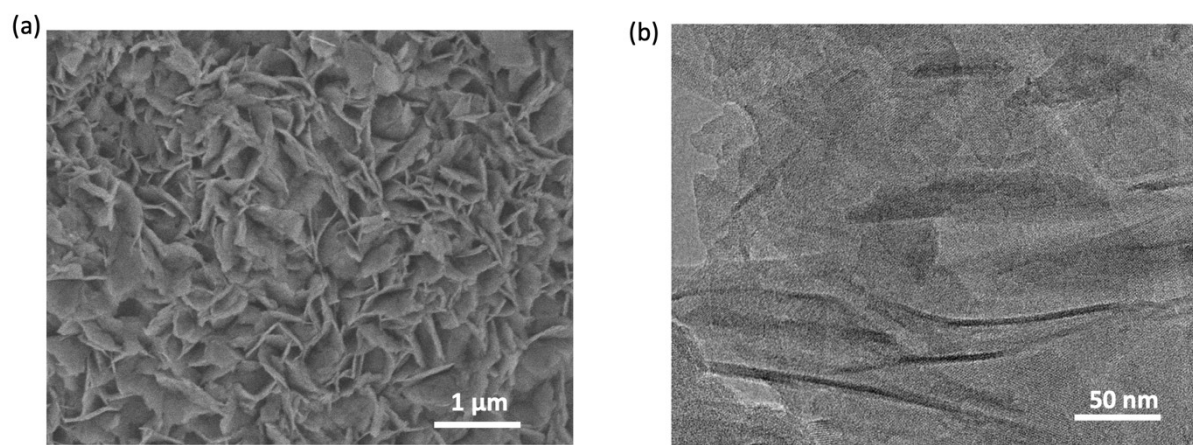**Figure S1.** PXRD patterns of MCM-22 samples.

Figure S2. (a) SEM and (b) TEM images of MCM-22 samples.
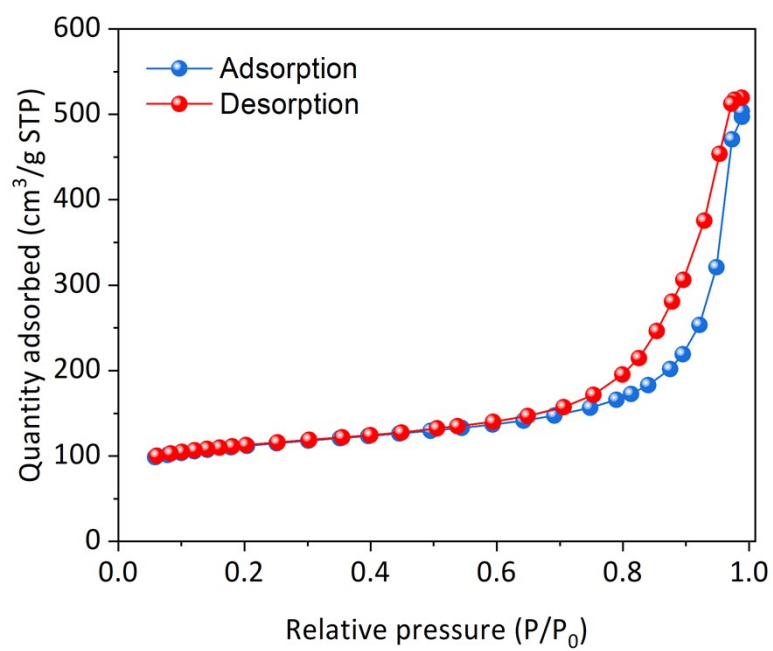
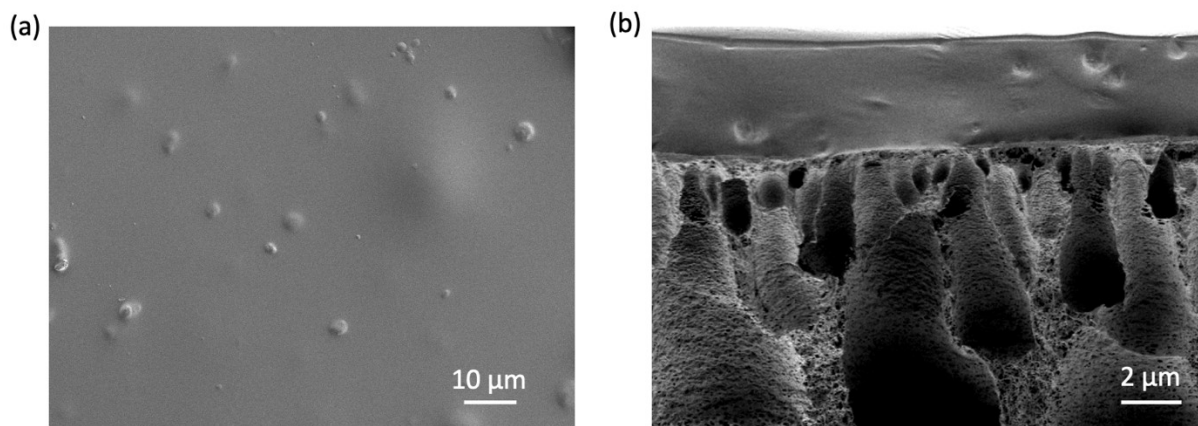**Figure S3.** Nitrogen adsorption and desorption isotherms of MCM-22 samples.

Figure S4. SEM images of (a) surface and (b) cross-section of organosiloxane membrane with 2 wt% MCM-22 loading.
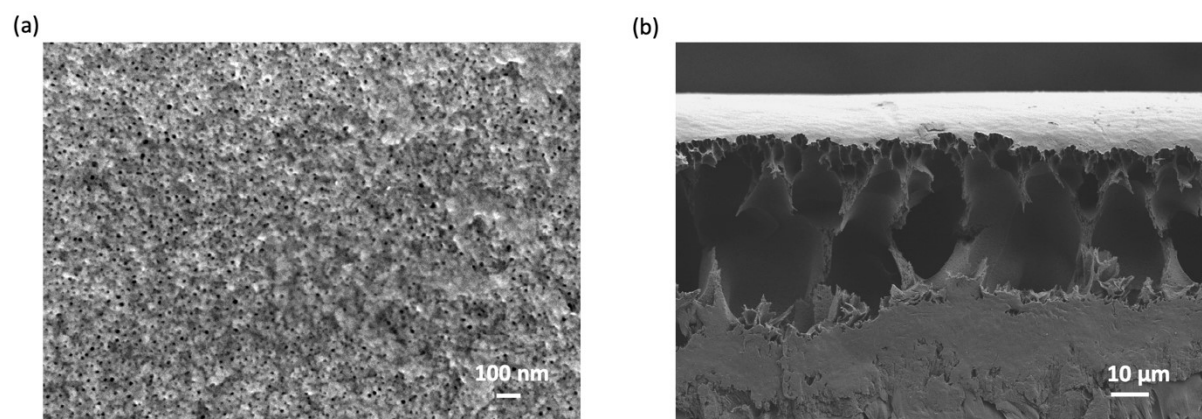
Figure S5. SEM images of (a) surface and (b) cross-section of PAN/non-woven cloth support.
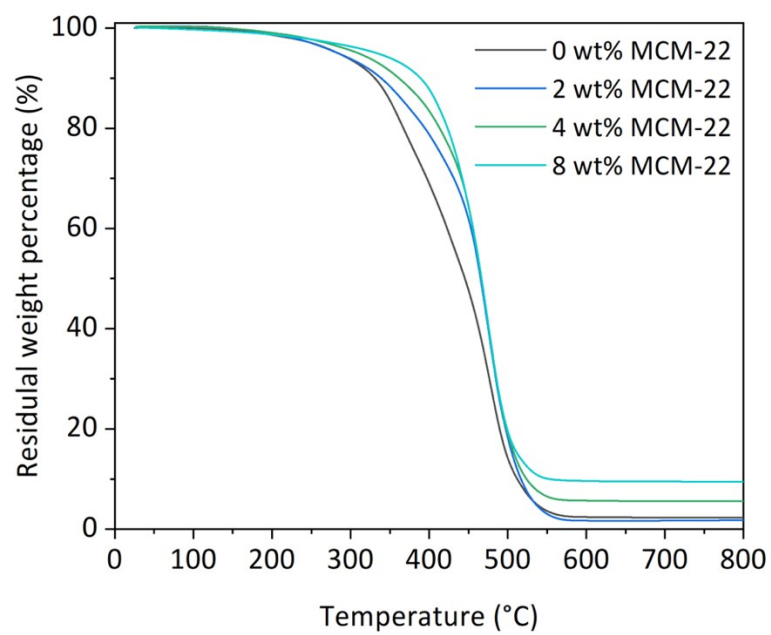
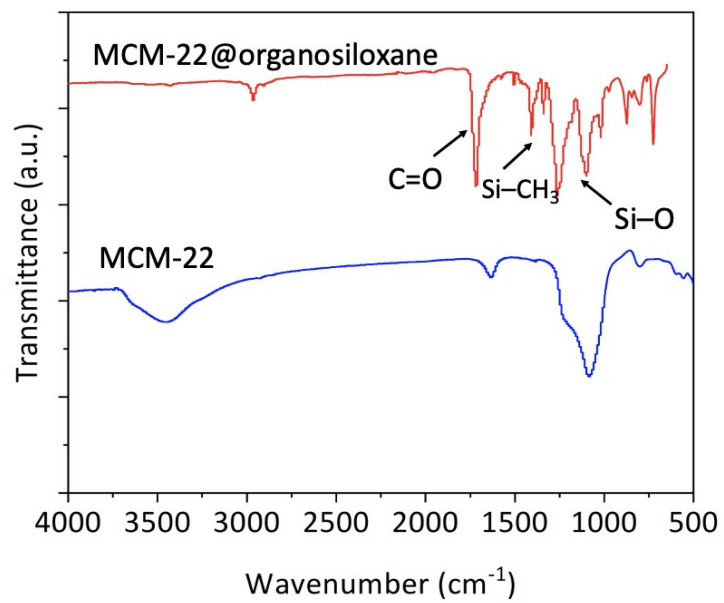**Figure S6.** TGA curves of self-standing MCM-22@organosiloxane membranes.

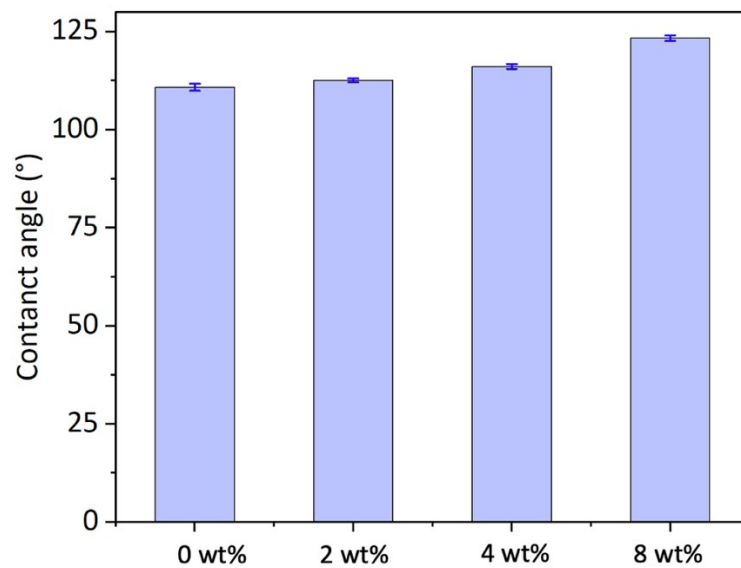**Figure S7.** FT-IR spectrogram of MCM-22 powders and MCM-22@organosiloxane membrane sample.

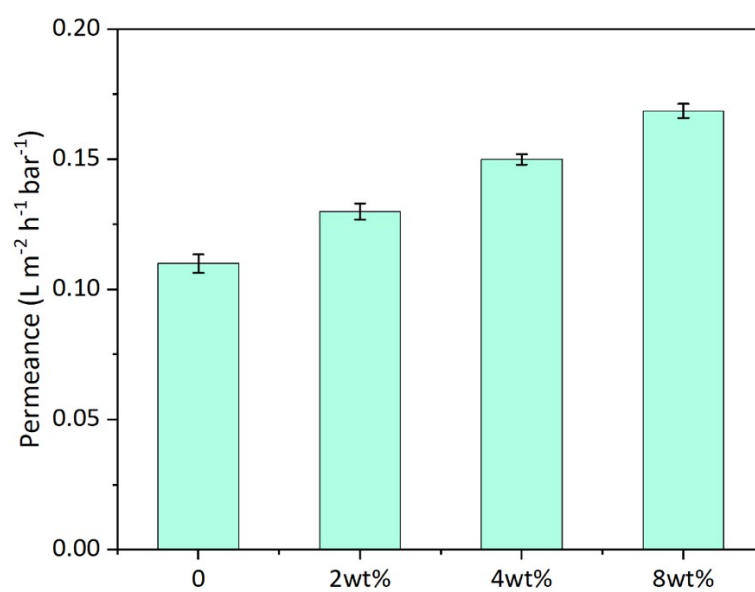**Figure S8.** Water contact angles of MCM-22@organosiloxane membranes.

Figure S9. The permeance of MCM-22@organosiloxane membranes with different filler loading.
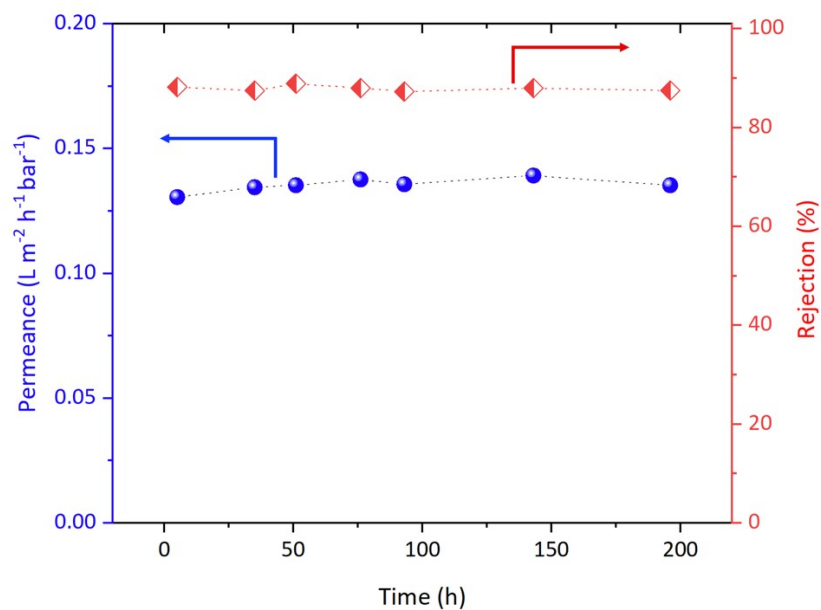
Figure S10. Separation performance of heavy aromatic oil solution at 30 °C and 3.0 MPa using MCM-22@organosiloxane membrane (2 wt% loading). The rejection rate of pentacyclic aromatic hydrocarbon was investigated.

Table S1. GC×GC-Flame-ionized detection (FID) analysis of heavy aromatic oil.

Components	weight percentage (wt%)
$C_{10}A$	48.7095
$C_{11}A$	8.6843
C_{12}^+A	2.7590
Naphthalene	6.8801
Methylnaphthalene	7.8685
Dimethylnaphthalene	4.1648
Polymethylnaphthalene	18.1709
Fluorene derivatives	2.0852
Tricyclic aromatic hydrocarbon	0.5927
Tetracyclic aromatic hydrocarbon	0.0659
Pentacyclic aromatic hydrocarbon	0.0190

Table S2. Separation performance of MCM-22@organosiloxane membranes.

Membranes	Rejection rate(%)			
	Fluorene derivatives	Tricyclic aromatic hydrocarbon	Tetracyclic aromatic hydrocarbon	Pentacyclic aromatic hydrocarbon
0 wt% MCM-22	24.2	29.3	43.2	76.4
2 wt% MCM-22	28.2	35.3	50.6	88.7
4 wt% MCM-22	27.3	33.6	47.4	82.6
6 wt% MCM-22	26.6	32.1	45.6	78.7
8 wt% MCM-22	24.7	30.4	44.1	77.5

Table S3. Organic solvent nanofiltration performance comparison with the state-of-the-art membranes.

Membrane (Material)	Organic Solvent	Temperature (°C)	Permeance ($L\ m^{-2}\ h^{-1}\ bar^{-1}$)	Molecular weight of marker ($g\ mol^{-1}$)	Rejection (%)	Ref.
Polytriazole	Crude oil	30	2.2	327	95	[3]
N-Aryl-linked spirocylic polymer	Crude oil	130	0.016	253	90	[4]
Polyamide $F_5N_6F_5$	Crude oil	30	4.2	395	90	[5]
Polyamide $F_9N_6F_9$	Crude oil	30	2.9	450	90	[5]
Polyamide $F_{13}N_6F_{13}$	Crude oil	30	0.9	420	90	[5]
Ogranosiloxane	Heavy aromatic oil	30	0.13	280	88	This work

References.

1. Y. Zhou, Y. Mu, M. F. Hsieh, B. Kabius, C. Pacheco, C. Bator, R. M. Rioux and J. D. Rimer, *J. Am. Chem. Soc.*, 2020, **142**, 8211-8222.
2. Z. Si, J. Li, L. Ma, D. Cai, S. Li, J. Baeyens, J. Degreve, J. Nie, T. Tan and P. Qin, *Angew. Chem. Int. Ed. Engl.*, 2019, **58**, 17175-17179.
3. S. Chisca, V. E. Musteata, W. Zhang, S. Vasylevskyi, G. Falca, E. Abou-Hamad, A. H. Emwas, M. Altunkaya and S. P. Nunes, *Science*, 2022, **376**, 1105-1110.
4. K. A. Thompson, R. Mathias, D. Kim, J. Kim, N. Rangnekar, J. R. Johnson, S. J. Hoy, I. Bechis, A. Tarzia, K. E. Jelfs, B. A. McCool, A. G. Livingston, R. P. Lively and M. G. Finn, *Science*, 2020, **369**, 310-315.
5. S. Li, R. Dong, V. E. Musteata, J. Kim, N. D. Rangnekar, J. R. Johnson, B. D. Marshall, S. Chisca, J. Xu, S. Hoy, B. A. McCool, S. P. Nunes, Z. Jiang and A. G. Livingston, *Science*, 2022, **377**, 1555-1561.