## **Supporting Information**

## Superhydrophobic MOFs decorated on hierarchically micro/nanofibrous membranes for high-performance emulsified oily wastewater separation and cationic dyes adsorption

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**Fig.S1.** <sup>1</sup>H NMR (in CDCl<sub>3</sub>) spectrum of UiO-66(NH<sub>2</sub>), modified UiO-66(NH<sub>2</sub>) and SMOFs.



Fig.S2. TEM images of the fibers of SMOFs@PT in high magnification.



Fig S3. (A) TEM images of the composite membranes with different content of MOFs incorporated (0%, 10%, 30%, 50%, and 70%). (B) The tensile stress-strain curves of the electrospun membranes incorporated with different content of MOFs (0%, 10%, 30%, 50%, and 70%). (C) Separation efficiency and flux of the composite membranes with different content of MOFs incorporated (0%, 10%, 30%, 50%, and

70%).



Fig S4. TGA curves of the as-prepared electrospun membranes (PT, SMOFs and SMOFs@PT)



**Fig.S5.** X-ray diffraction spectrum of the UiO-66(NH<sub>2</sub>), SMOFs nanoparticles, the pure PLLA, UiO-66(NH<sub>2</sub>)@PT and SMOFs@PT electrospun membranes.



**Fig.S6** Stress-strain curve of the PT, UiO-66(NH<sub>2</sub>)@PT and SMOFs@PT before and after oil-water separation.



**Fig.S7.** Separation efficiency  $(A_1-D_1)$  and flux  $(A_2-D_2)$  of the composite electrospun membranes (PT, UiO-66(NH<sub>2</sub>)@PT, modified UiO-66(NH<sub>2</sub>)@PT and SMOFs@PT) in different kinds of oil-water mixture.



**Fig.S8.** The effect of porous fibers on separation efficiency and flux of the patterned electrospun membranes.



**Fig.S9.** The cycling experiment of the as-prepared membranes (PT, UiO-66(NH<sub>2</sub>)@PT, modified UiO-66(NH<sub>2</sub>)@PT and SMOF@PT) against filtration time for the separation of emulsified oily wastewater.



**Fig.S10.** The cationic dye adsorption behavior of the PT, UiO-66(NH<sub>2</sub>)@PT and modified UiO-66(NH<sub>2</sub>)@PT with the increase of time:  $(A_1, B_1, C_1)$  Optical images of the color change of the filtrates. The UV-vis spectra collected each 3 h during the adsorption process of RhB ( $A_2$ ,  $B_2$ ,  $C_2$ ) and MB ( $A_4$ ,  $B_4$ ,  $C_4$ ). The statistical analysis of the RhB ( $A_3$ ,  $B_3$ ,  $C_3$ ) and MB ( $A_5$ ,  $B_5$ ,  $C_5$ ) residual concentration in the filtrates.



Fig.S11. The Zeta potential change of the SMOFs nanoparticles with the increase of the cationic dyes added.

**Table S1.** Comparison of the separation performance of emulsified oily wastewater by

 the membranes reported in the literatures and prepared in this work.

Types	Materials	Operation	Separation	Flux	Dof
	description	Method/	efficiency	$(L \bullet m^{-2} \bullet h^{-1})$	Kei

		Pressure			
		(bar)			
polymeric electrospun membranes	PAN nanofibrous membrane with a biomimetic and sub- micrometer porous skin layer	Dead end / Gravity	>99.93%	312-5152	[54]
	A nanofibrous composite membrane consisting of a nonwoven PAN nanofibrous supporting layer and a thin PVA hydrophilic barrier layer	Cross-flow/ 0.2 MPa	99.6%	347.81	[55]
	A biomimetic nanofibrous membrane with BiOBr microspheres anchored on the SiO <sub>2</sub> /polyaniline (PANI) core–shell fibers.	Dead end / Gravity		6140	[59]
Polymeric electrospun membranes modifying with ingoranic particles	A PLA-based electrospun membrane with homogeneous dispersion of maghemite γ- Fe <sub>2</sub> O <sub>3</sub> nanoparticles on the fiber surface and dual-scaled micro/nanopores in membrane.	Dead end/ Gravity		2925	[1]
	The surface of the PLA membranes was spinned with TiO <sub>2</sub> particles	Dead end / 1 MPa		102	[58]
	The surface of the membranes was polymerized with F-PBZ functional layer that incorporated SiO <sub>2</sub> NPs.	Dead end / Gravity			[79]

	A nanofibrous polyacrylonitrile membrane decorated with UiO-66(NH <sub>2</sub> ).	Dead end / Gravity	>99%	2107	[2]
	The PAN membranes with ZIF-8 nanoparticles incorporated.	Dead end / Gravity	>99%	>900	[7]
Polymeric membranes modifying with metal	The MOFs was loaded on the surface of stainless steel mesh through PDA modification technology	Dead end / Gravity		350	[47]
frameworks	The membrane surface was decorated by UiO-66(NH <sub>2</sub> )	Dead end / 0.1 MPa	>86%	2330	[14]
	The patterned membranes constructed with porous fibers, in which the superhydrophobic SMOFs were incorporated.	Dead end / Gravity	>99%	>15000	This work