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Supporting Information for

MOF-membrane based on covalent bonding driven assembly of NMOF with organic oligomer and its application for membrane reactor

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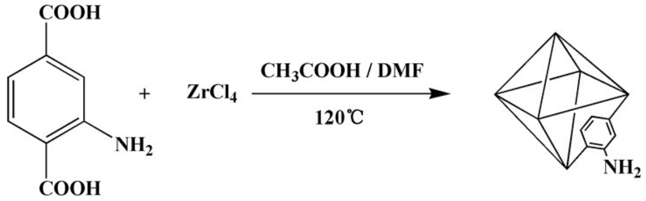
Content

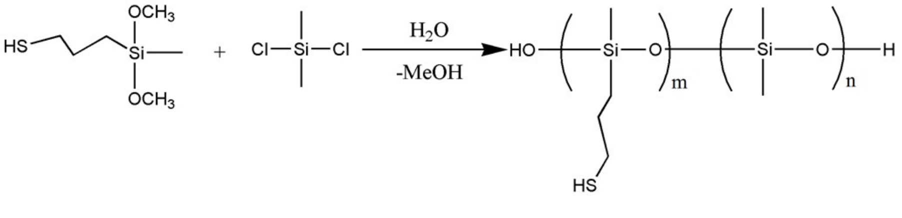
1. Materials and instrumentation. All the chemicals were obtained from commercial sources (Acros) and used without further purification. Infrared (IR) spectrums were obtained in the 400-4000 cm^{-1} range using a Bruker ALPHA FT-IR Spectrometer. Elemental analyses were performed on a Perkin-Elmer model 2400 analyzer. ^{1}H NMR data were collected on a Bruker Avance-300 spectrometer. Chemical shifts are reported in δ relative to TMS. Thermogravimetric analyses were carried out on a TA Instrument Q5 simultaneous TGA under flowing nitrogen at a heating rate of 10°C/min. XRD pattern was obtained on D8 ADVANCE X-ray powder diffractometer (XRPD) with Cu Kα radiation (λ = 1.5405 Å). The scanning electron microscopy (SEM) micrographs were recorded on a Gemini Zeiss Supra TM scanning electron microscope equipped with energy-dispersive X-ray detector (EDS). The CO_2 adsorption-desorption isotherms were performed on an ASAP 2020/TriStar 3000 (Micromeritics) using CO_2 adsorption at 273 K. The concentration of dyes were measured using a UV/Vis spectroscopy (TU-1900Beijing PuXi). ICP measurement was performed on an IRIS Interpid (II) XSP and NU AttoM. The contact anagles were obtained on Dataphysics OCA-20 contact angle analyzer. The nano-sized UiO-66-NH_2 was prepared according to the reported method.[1]

2. Synthesis of UiO-66-NH_2 NMOF[1]



$ZrCl_4$ (93.2 mg, 0.4mmol) and 50 equiv of acetic acid (1200 mg, 20 mmol) were dissolved in DMF (16 mL) by using ultrasound for about 10 min. The linker 2-aminoterephthalic acid (72.5 mg, 0.4mmol) was added to the clear solution in an equimolar ratio with regard to $ZrCl_4$. The tightly capped flasks were kept in an oven at 120°C under static conditions. After 24 h, the reaction system was cooled to room temperature and the precipitate were isolated by centrifugation. The solid were suspended in fresh DMF (10 mL). After standing at room temperature for 5h, the suspension were centrifuged and the solvent were decanted off. The obtained particles were washed with ethanol (10 mL) for several times in the same way as described for washing with DMF. Finally, the solids were dried under reduced pressure to obtain 120 mg of the as synthesized UiO-66-NH_2 crystals.

3. Synthesis and characterization of thiol side chain attached poysiloxane oligomer



Thiol side chain decorated polysiloxane (PSI-SH) was synthesized according to the literature method.[2] Dimethyldichlorosilane (5 mL), 3-mercaptopropylmethyldimethoxysilane (5 mL), and *p*-toluenesulfonic acid (2.0 mg) were orderly added to a 50 mL round-bottom flask with deionized water (3 mL). The reaction was conducted at 50°C for 48 h with magnetic stirring. The product was then extracted by diethyl ether. After removing the solvent in vacuum, the product was obtained as oil. ^{1}H-NMR (300MHz, $CDCl_3$): δ = 0.01 - 0.25 (m, -Si*CH*$_3$), 0.60 - 0.75 (m, -Si*CH*$_2$CH$_2$CH$_2$SH), 1.31 (s, -*SH*), 1.60 - 1.75 (m, -SiCH$_2$*CH*$_2$CH$_2$SH), 2.55 - 2.60 (m, -SiCH$_2$CH$_2$*CH*$_2$SH). The gel permeation chromatography (GPC) data of PMMS was listed in Table S1.

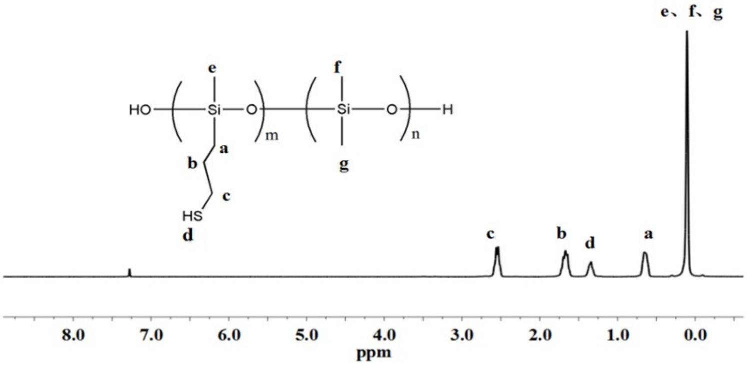


Fig. S1 ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of thiol side chain decorated polysiloxane.

Table S1. Molecular weight of the obtained PSI-SH

Mn	Mw	MP	polydispersity
1476	1815	1689	1.23

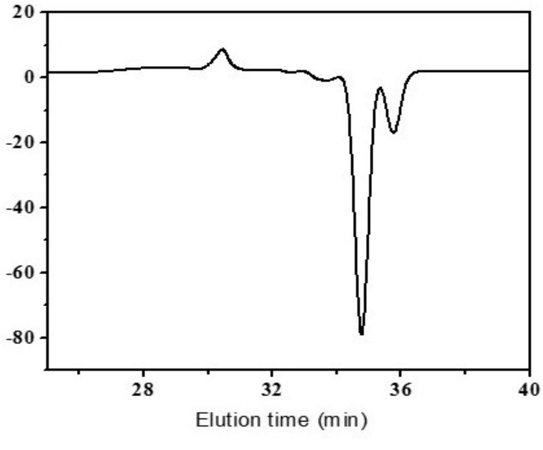
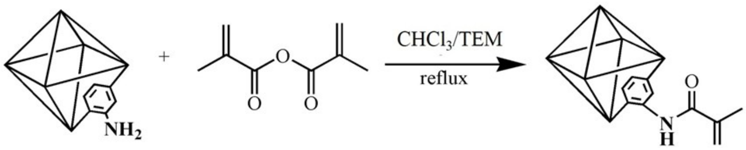


Fig. S2 GPC trace for PSI-SH.

4. Synthesis and characterization of UiO-66-NH-Met



UiO-66-NH$_2$ (600 mg, ca. 2mmol -NH$_2$) was suspended in 50 mL anhydrous CHCl$_3$. Redistilled trimethylamine (TEM, 1 equiv) and methacrylic anhydride (2.36 mL, 16 mmol, 8 equiv) were added to above solution. The mixture was stirred at 55°C for 24 h, after which the solvent was decanted, and fresh CHCl$_3$ was added for the subsequent washing and soaking to rinse the crystals free of any excess impurity. Finally, the solids were dried under reduced pressure to generate the UiO-66-NH-Met nanocrystals.

The post-synthetic modification of UiO-66-NH$_2$ was confirmed by ^{1}HNMR. The ^{1}H-NMR spectrum performed on dilute acid digested MOF samples confirmed the formation of methyl propenyl group. In addition, the modification yield was determined to be 94 % based on the ^{1}H NMR spectrum (Figure S3).

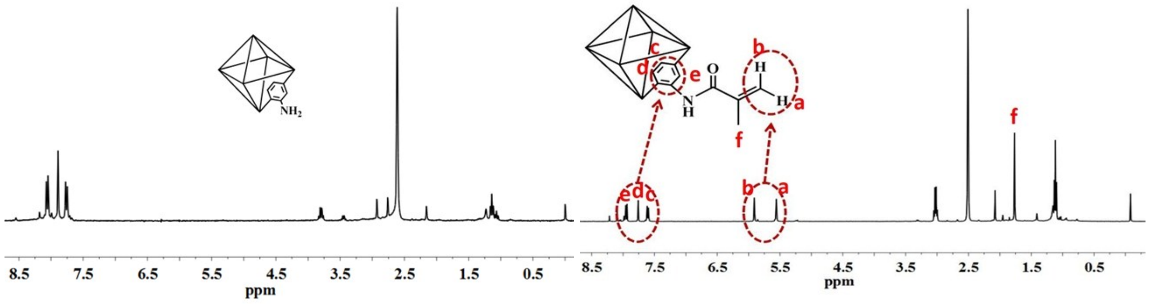


Fig. S3 ^{1}H-NMR (300 MHz, DMSO-d^6) spectra of UiO-66-NH$_2$ and UiO-66-NH-Met. In the ^{1}H NMR spectrum of UiO-66-NH-Met, the peaks at 5.86, 5.56 and 1.77 ppm are attributed to protons of a, b, and c on methacrylamide group. Meanwhile, the peaks at 7.67, 7.87 and 8.17 ppm are corresponding to the phenyl protons. The peak area ratios of a/b/c/d/e/f = 1.00/1.00/1.06/1.02/1.03/3.02. So the modified yield is at least 1/1.06 = 94 %.

5. Synthesis and characterization of UiO-66-TEM (1)

UiO-66-NH-Met (0.2 g) and photoinitiator of 2, 2-dimethoxy-2-phenyl acetophenone (20 mg) were added to a CHCl$_3$ solution (10 mL) of PSI-SH (0.13 g). After sonicated for 5 min, the mixture was stirred at room temperature for 0.5 h. The resulting suspension was dripped into a rounded Teflon mould and photopolymerization under a UV lamp (365 nm) for ca. 1 h to generate light yellow membrane. The obtained free-standing membrane was dried in vacuum at 60°C for 1 h. The Zr content in **1** is 12.09 % (calculated 11.88 %) (Table S1). So the doping amount of UiO-MOF is up to 60 wt %.

For further confirmation of this post-synthesis, the reaction of methacrylic anhydride decorated dimethyl amino-terephthalate (**A**) and PSI-SH was examined before the post-synthetic polymerization of UiO-66-NH-Met via polysiloxane oligomer. The reaction proceeded quite smoothly under the same reaction conditions, and the expected product (**B**) was well confirmed by the ^{1}H NMR spectra.

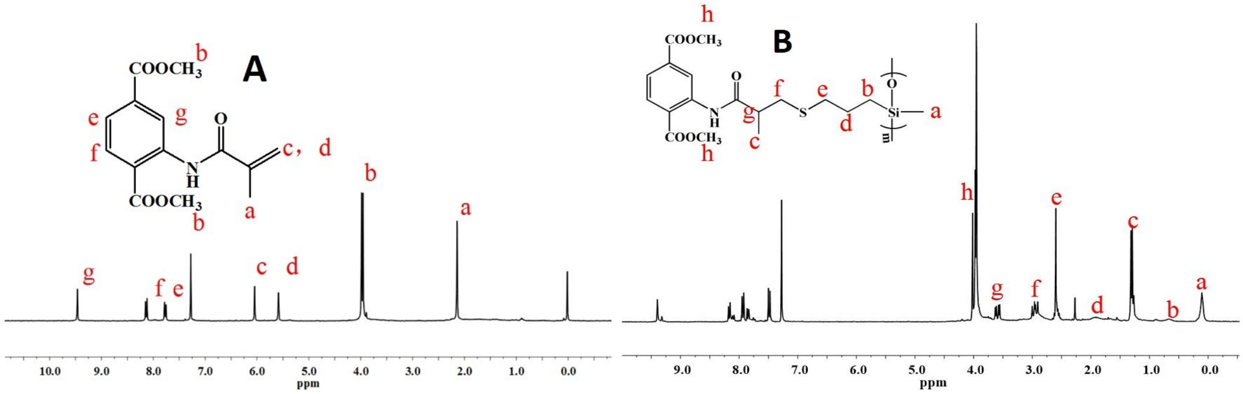


Fig. S4 ^{1}H-NMR (300 MHz, $CDCl_3$) spectra of **A** and **B**. The single peak at 1.31 ppm for -SH (Fig. S1) and the peaks at 6.05 and 5.59 ppm for $-C=CH_2$ disappeared, indicating the formation of the desired polymerized product **B**.

6. Synthesis and characterization of Au(0)@UiO-66-TEM (2)

1 (100 mg) was added to an EtOH (10 mL) solution of chloroauric acid (100 mg, 1.0 mmol). The mixture was stood for 8 h at room temperature. The resulting membrane was washed with fresh EtOH (3 times) and dried in air. The Au(III) loaded membrane was soaked in an aqueous solution (10 mL) of $NaBH_4$ (20 mg, 0.52 mmol) for 0.5 h. The resulting membrane was washed with fresh water (2 times) and dried in air to afford **2** as dark brown membrane. Inductively coupled plasma (ICP) measurement indicated that the encapsulated amount of Au NPs in **2** is 2.71 wt % (Table S2).

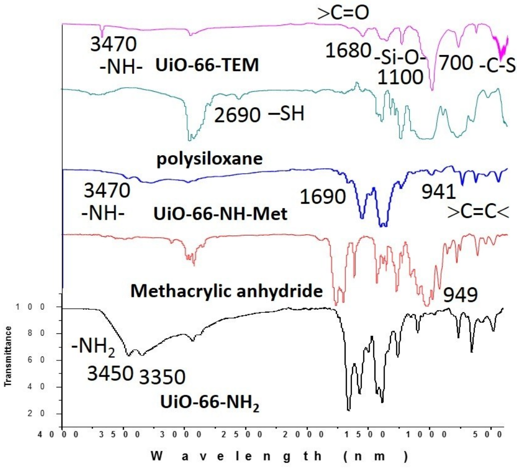


Fig. S5 IR spectra of UiO-66-NH_2, methacrylic anhydride, UiO-66-NH-Met, polysiloxane and UiO-66-TEM (**1**).

Table S2. ICP results for **1** and **2**.

Sample	conc. (mg/L)		Zr 339.198 mg/L	Zr 257.139 mg/L	Zr 272.262 mg/L	**Zr %**
1		1	18.5964	18.9213	18.2365	
		2	18.8027	19.1069	19.4755	
	156	<x>	**18.6996**	**19.0141**	**18.856**	**12.09**

Sample	conc. (mg/L)		Zr 339.198 mg/L	Zr 257.139 mg/L	Zr 272.262 mg/L	**Zr %**	Au 267.595 mg/L	Au 197.819 mg/L	Au 201.265 mg/L	**Au %**
2		1	25.3479	25.302	25.0515		5.75485	5.76584	5.81639	
		2	25.3821	25.1129	24.9595		5.68588	5.69762	5.72318	
	212	<x>	**25.365**	**25.2074**	**25.0055**	**11.88**	**5.720365**	**5.73173**	**5.769785**	**2.71**

7. Knoevenagel condensation of 4-nitrobenzaldehyde with dicyanopropane catalyzed by 1

Batch experiment. The reaction was carried out by combination of 4-nitrobenzaldehyde (38 mg, 0.25 mmol) and dicyanopropane (19 μL, 0.30 mmol) in the presence of **2** (6.5 mg) in MeOH (3.5 mL) at room temperature. The reaction readily proceeded (monitored by GC) and the reaction was finished within ca. 8 min (yield, 97 %). The membrane can be reused for five catalytic runs. After each catalytic run, the membrane pieces were collected, washed with MeOH and dired in air.

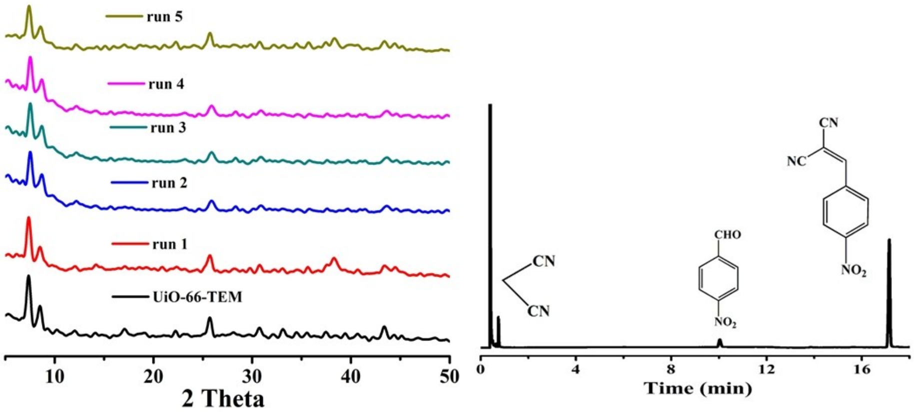


Fig. S6 Left: the XRPD patterns of **1** and it after five catalytic runs. Right: gas chromatography for the knoevenagel condensation reaction catalyzed by **1** at ca. 8 min. The reaction is clean and the yield is up to 97 % based on GC analysis.

Continuous flow-through operation for Knoevenagel condensation. In the continious flow-through condensation experiemnt, the MeOH (35 mL) solution of 4-nitrobenzaldehyde (380 mg, 2.5 mmol) and dicyanopropane (190 μL, 3.0 mmol) was pumped through a piece of UiO-66-TEM (**1**) membrane (14 mg, diameter 13 mm, effective area 81 mm^2) using a peristaltic pump. Flow rate of 1 mL/min was used to realize the MeOH reaction system circulation. The reaction system was periodically detected by GC analysis and the reaction was finished in ca. 60 min. The condensing product precipitated out from the reaction solution and was collected by the membrane filter.

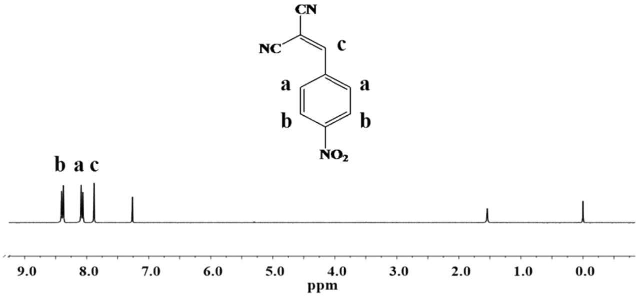


Fig. S7 ^{1}H-NMR ($CDCl_3$, 300 MHz) of the condensation product precipitated out from the reaction solution.

Table S3. ICP results for **1** after flow-through catalytic operation

Sample	conc. (mg/L)		Zr 339.198 mg/L	Zr 257.139 mg/L	Zr 272.262 mg/L	**Zr %**
1 after use		1	19.1282	18.8729	18.7827	
		2	19.4351	18.7867	18.7832	
	162	<x>	**19.2816**	**18.8298**	**18.783**	**11.71**

8. 4-NP reduction catalyzed by 2

Batch experiment. The experiemnt was performed using $NaBH_4$ as hydrogen source. **2** (6.5 mg, 8.9×10^{-2} mmol % Au) was soaked in a freshly prepared aqueous solution (2.75 mL) of 4-NP (7.0×10^{-2} mM) with $NaBH_4$ (5.72mg，0.15mmol) at ambient temperature. The reaction process was monitored by UV-vis spectrum. After each catalytic run, **2** was collected by filtration. After washed with MeOH and dired in air, **2** was directly resused for the next catalytic run.

Continuous flow-through operation for 4-NP reduction. The continuous flow-through 4-NP reduction was performed in a similar way to that of Knoevenagel condensation. In a typical experiment, the aqueous solution (55 mL) of 4-NP (7.0×10^{-2} mM) and $NaBH_4$ (114.4 mg，3.0 mmol) was driven by the peristaltic pump to continuously pass through the Au-loaded membrane **2** (effective area 81 mm^2, 8.9×10^{-2} mmol % Au) at a flow rate of 1 mL/min. The 4-NP reduction reaction was monitored by UV-vis spectrum and the reaction system was quantified by periodically collecting the filtrate and measuring its UV-light adsorption. The complete 4-NP degradation was achieved in ca. 65 min.

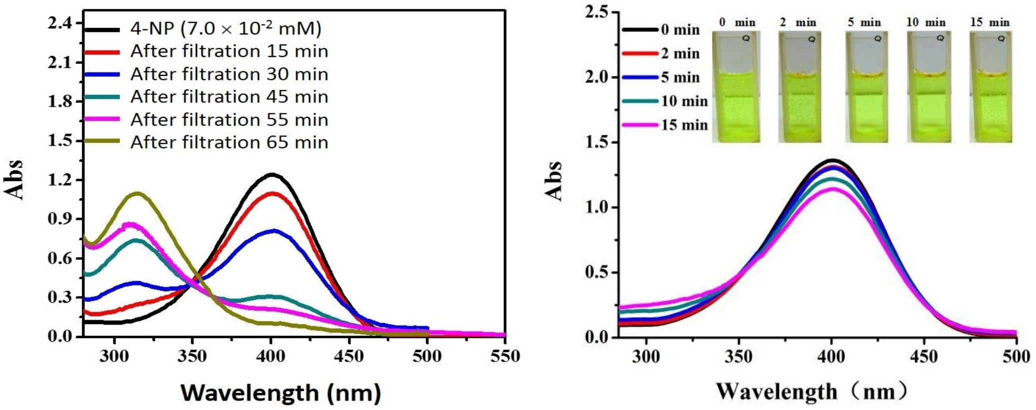


Fig. S8 Left: time dependent UV-vis adsorption spectra for the reduction of PNP catalyzed by **2** in the continuous flow-through operation at room temperature. Right: no effective 4-NP reduction occourred in the presence of **1**, indicating that the Au NPs in **2** are the active catalytic sites.

Table S4. ICP results for **2** after flow-through catalytic operation

Sample	conc. (mg/L)		Zr 339.198 mg/L	Zr 257.139 mg/L	Zr 272.262 mg/L	**Zr %**	Au 267.595 mg/L	Au 197.819 mg/L	Au 201.265 mg/L	**Au %**
2 after use		1	17.9512	17.0945	17.0885		4.1145	4.0884	3.95925	
		2	17.5595	17.0045	17.0047		4.25963	4.18022	4.06718	
	154	<x>	**17.7554**	**17.0495**	**17.0466**	**11.22**	**4.18706**	**4.13431**	**4.01321**	**2.66**

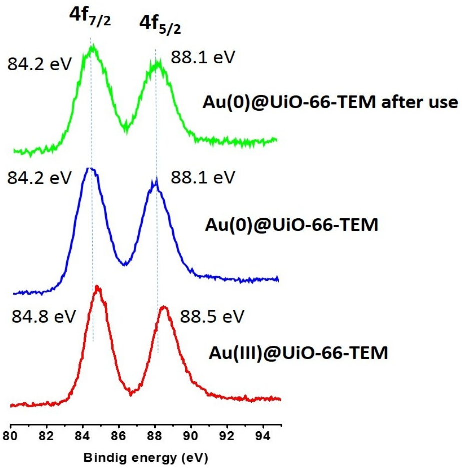


Fig. S9 XPS spectra of Au(III)@UiO-66-TEM and Au(0)@UiO-66-TEM (**2**) and it after use.

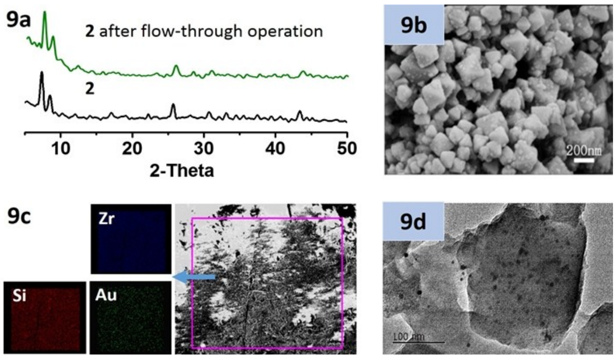


Fig. S10 (a) XRPD patterns of **2** and it after the flow-through operation. (b) SEM image of **2** after the flow-through operation. (c) Corresponding SEM-EDX images of Zr, Si and Au images. (d) TEM image of **2** after the flow-through operation.

9. Contact angle (CA) measurement

The contact angle (CA) values were obtained by measuring more than five different positions of the same sample at 25°C using the sessile drop method on a contact angle meter. DI water was used as the test liquid, and DI water droplets of 20 μL was put on the membrane surface. The image of the drop was calculated from the sharp of the drop (both left and right contact angles) with an accuracy of ±0.1° by using an image analysis system.

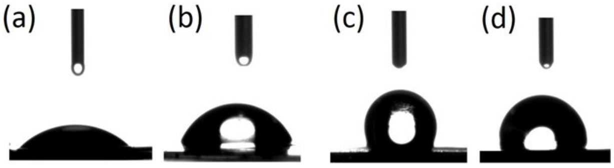


Fig. S11 Contact angles of the sample: (a) UiO-66-NH_2, (b) UiO-66-NH-Met, (c) silicone oil and (d) UiO-66-TEM.

Table S5. Abbreviation of the sample names in this manuscript

Samples	Abbreviation
Methacrylamide group decorated UiO-66-MOF NPs	UiO-66-NH-Met
Homogeneous UiO-66-based membrane	UiO-66-TEM (**1**)
Au(0)-loaded MOF-polymer composite membrane	Au(0)@UiO-66-TEM (**2**)
Thiol side chain functionalized polysiloxane oligomers	PSI-SH
4-nitrophenol	4-NP
4-aminophenol	4-AP

10. References

1. J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K. P. Lillerud, *J. Am. Chem. Soc.,* 2008, **130**, 13850-13851.

2. Y. Zuo, J. Gao, S. Feng, *Adv. Funct. Mater.,* 2015, **25**, 2754-2762.