*Electronic Supplementary Information for*

# Microporous organic network@PET hybrid membranes: Removal of minute organic pollutants dissolved in water

*Eui Soon Kim,[a] Ju Hong Ko,[a] Sang Moon Lee,[b] Hae Jin Kim,[b] and Seung Uk Son*[a]*

*[a]Department of Energy Science and Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea*

*[b]Korea Basic Science Institute, Daejeon 350-333, Korea*

## *Experimental Sections*

SEM and TEM images were obtained using a FE-SEM (JSM6700F) and a JEOL 2100F unit operated at 200kV, respectively. The $N_2$ adsorption-desorption isotherm (77 K) was measured using a BELSORP II-mini equipment. The Kr adsorption-desorption isotherm (77 K) was measured at the Korea Basic Science Institute (Daejeon, South Korea). Pore size analysis was performed by the DFT method. PXRD patterns were obtained using a Rigaku MAX-2200 operating with filtered Cu-Ka radiation. Infrared absorption spectra were recorded using a Bruker VERTEX 70 FT-IR spectrometer. The absorption spectra were obtained from diffuse reflectance spectroscopy using a SHIMADZU UN-3600. The solid phase $^{13}$C-NMR spectroscopy (CPTOSS) was conducted using a 500 MHz Bruker ADVANCE II NMR spectrometer at the NCIRF of Seoul National University utilizing a 4 mm magic angle spinning probe. The water contact angles of PET and MON@PET membranes were measured using a Theta Optical Tensiometer model (KSV instruments, Ltd.) and electrooptics comprising a CCTV camera connected to a computer (software Attension Theta). The contact angle of the model MON materials was measured using a pellet of powdery sample. UV-vis absorption spectra were obtained using a JASCO V-630.

## *Synthetic procedure for MON@PET membranes*

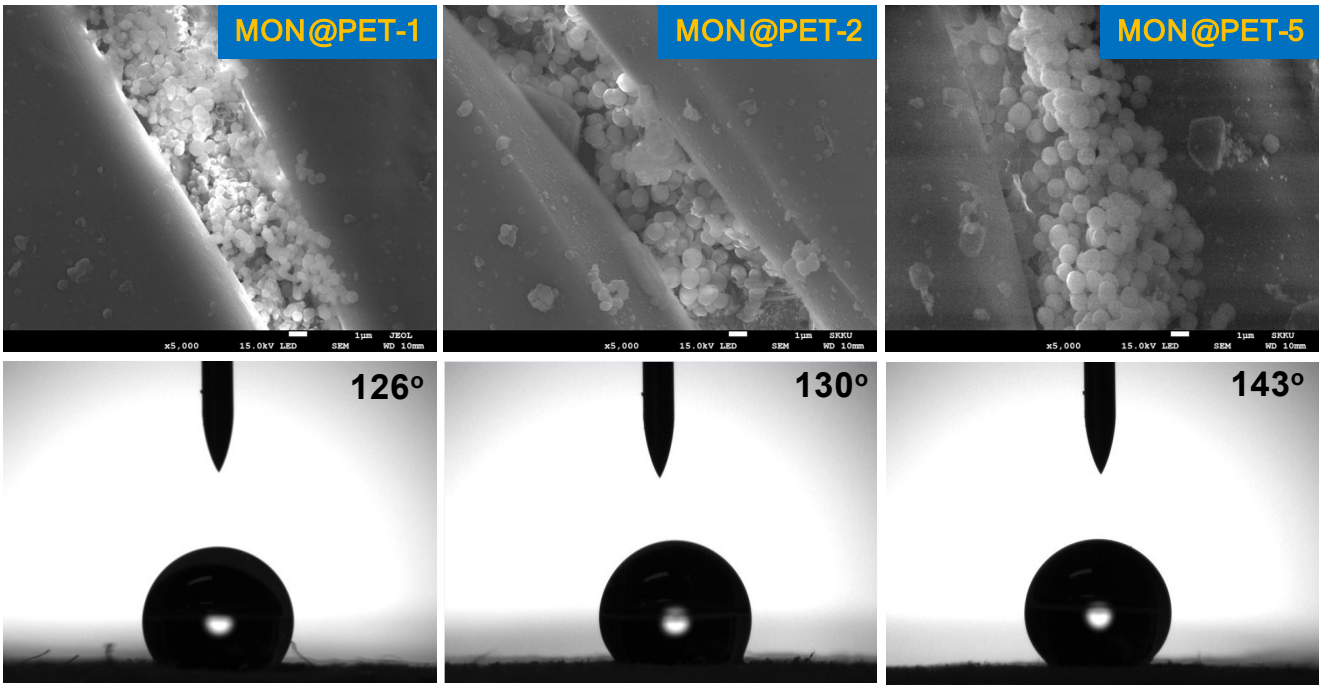
Tetrakis(4-ethynylphenyl)methane was prepared following the synthetic procedure in the literature (refer to S. Yuan, S. Kirklin, B. Dorney, D. –J. Liu and Luping Yu, *Macromolecules* 2009, **42**, 1554-1559). The PET membranes (disc shape with a 2.5 cm diameter) were prepared by the detaching the PAN part of PAN0225100 (Sterlitech Co. USA). The PET membrane was added to a 50 mL flame dried Schlenk flask, followed by adding $(PPh_3)_2PdCl_2$ (17 mg, 0.024 mmol), CuI (4.4 mg, 0.023 mmol), and toluene (10 mL). The reaction mixture was sonicated for 1 h. Tetrakis(4-ethynylphenyl)methane (0.10 g, 0.24 mmol), 1,4-diiodobenzene (0.16 g, 0.48 mmol), and diisopropylamine (20 mL) were added. The reaction mixture was heated at 90 $^{o}$C for 1 day, 2 days, 3 days, and 5 days for the preparation of MON@PET-1, MON@PET-2, MON@PET-4, and MON@PET-5, respectively. The resultant MON@PET membrane was retrieved and washed with methylene chloride and methanol. The membrane was dried in an oven at 60 $^{o}$C overnight. The average weight of original PET membranes (disc shape with a 2.5 cm diameter) was measured as 49.9±1.0 mg. After loading MON materials on the PET, the average weight of MON@PET-3 was measured as 52.0±0.9 mg. The model MON materials were retrieved from the reaction mixture through centrifugation, washed with methylene chloride, methanol, and acetone, and dried under vacuum.

***Procedure of filtration studies***

MON@PET membrane was cut to a disc shape with a 1.3 cm diameter using a puncher (Electrode Punching Tool WC-H125, Wellcos Co.). The disc was set on the syringe filter holder (T14N17619, Milipore Co.). Nitrobenzene was dissolved in water to prepare solutions with the concentrations of 3.9, 7.8, 15.6, and 31.2 ppm. 4-Methylanisole, benzaldehyde, acetophenone, phenol, benzyl alcohol, 1,4-hydroquinone, and benzoic acid (7.8 ppm) were dissolved in water. To be accurate tests, we prepared mother (100 ppm) solution and diluted the mother solution by adding water to prepare the target concentration. To prepare 3.9 ppm solution, 24.60 g of water was added to the 1.00 mL of mother solution which was weighted as 1.00 g. To prepare 7.8 ppm solution, 23.60 g of water was added to the 2.00 mL of mother solution which was weighted as 2.00 g. To prepare 15.6 ppm solution, 21.60 g of water was added to the 4.00 mL of mother solution which was weighted as 4.00 g. To prepare 31.2 ppm solution, 22.00 g of water was added to the 10.00 mL of mother solution which was weighted as 10.00 g. The model organic pollutant solution (5 mL) in a syringe was passed through the filter for 1 min, 30 s, 15 s, and 7 s with a syringe pump (linear force 13.6 kg) and hand pressure. The filtered solution was analyzed by UV-vis absorption spectroscopy. In the case of 15.6, and 31.2 ppm, the filtered solutions were diluted by 4 and 8 times by addition water. The concentration of the filtered solution was determined using the intensity values of model solution and the filtered solution at a fixed wavelength (nitrobenzene: 268 nm, 4-methylanisole: 275 nm, benzaldehye: 249 nm, acetophenone: 245 nm, phenol: 270 nm, benzyl alcohol: 204 nm, 1,4-hydroquinone: 288 nm, benzoic acid: 225 nm) based on the Beer-Lambert law. For reuse tests, the recovered membrane was washed by acetone, methylene chloride, and methanol and dried in an oven at 60 $^{o}$C overnight. The membrane was used for the next filtration.

**Fig. S1** (a) SEM images and contact angles of MON@PET-1, MON@PET-2, and MON@PET-5 hybrid membranes and (b) additional SEM images of MON@PET-3.

**(a)**




**(b)**

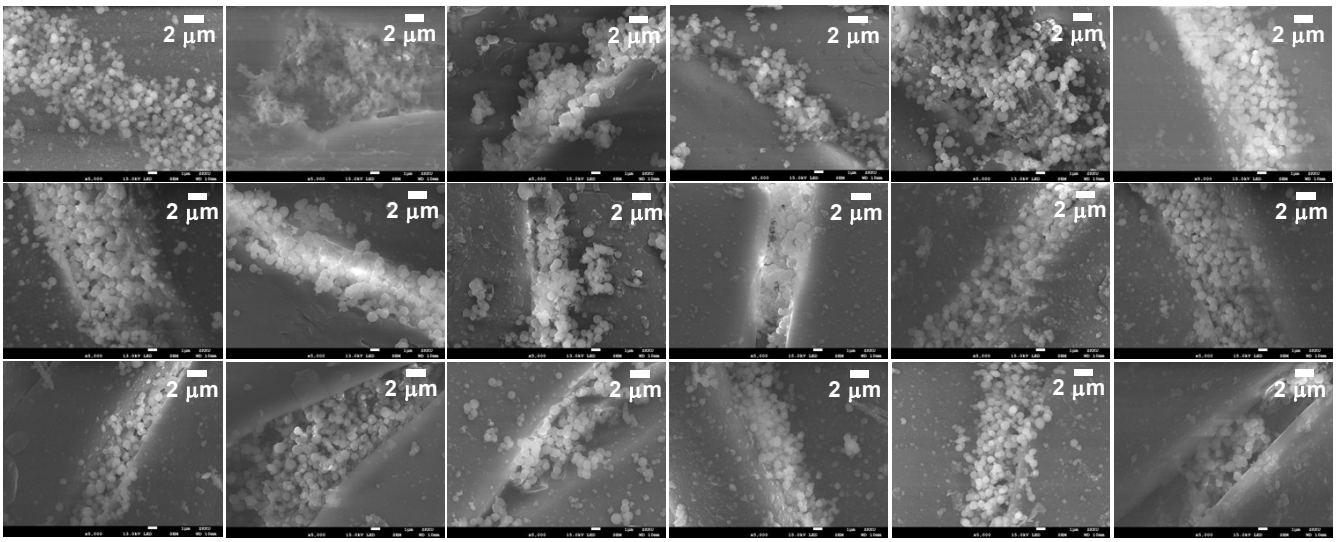


**Fig. S2** Powder X-ray diffraction studies of PET, MON@PET, and control MON materials.

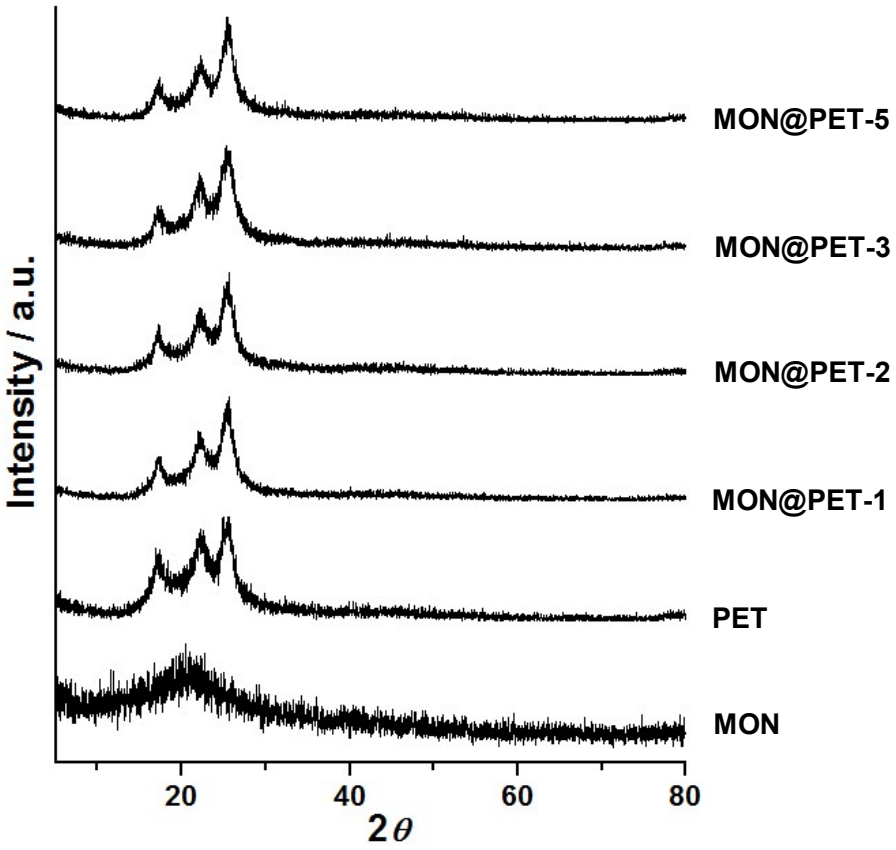



**Fig. S3** (a) Absorption (converted from reflectance spectra) and (b) IR absorption spectra of MON@PET-3 before and after five successive filtration of nitrobenzene.

**(a)** **(b)**

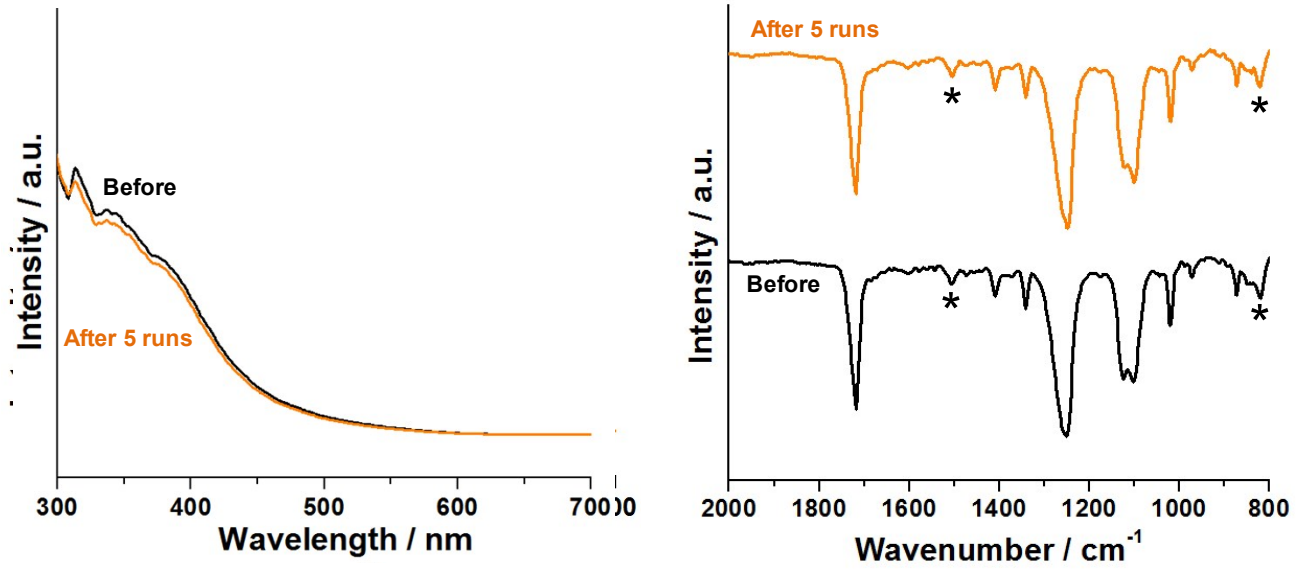
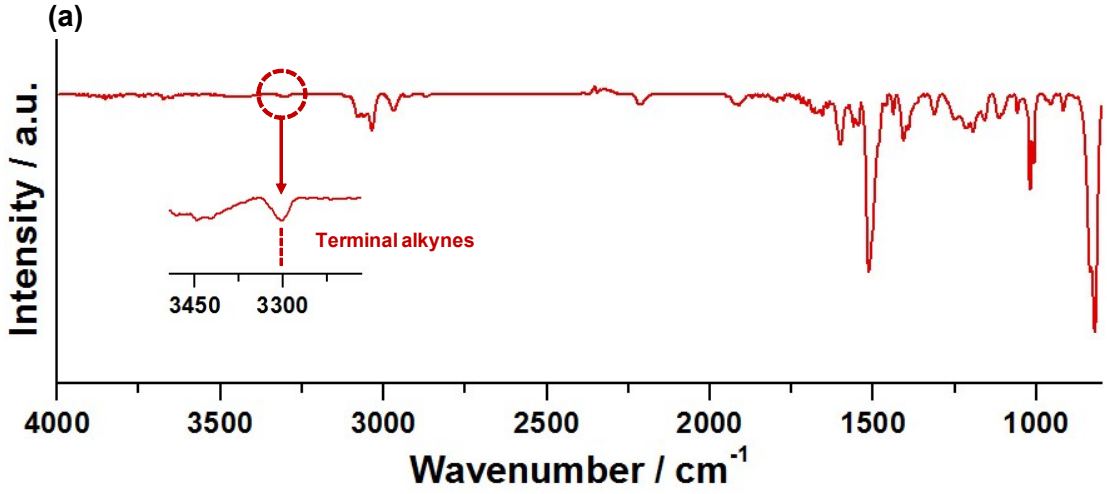



**Fig. S4** (a) IR spectrum of MON powder (pellet form) and (b) EDS spectra of MON powder and MON-PET-3, showing the connection defects in MON.



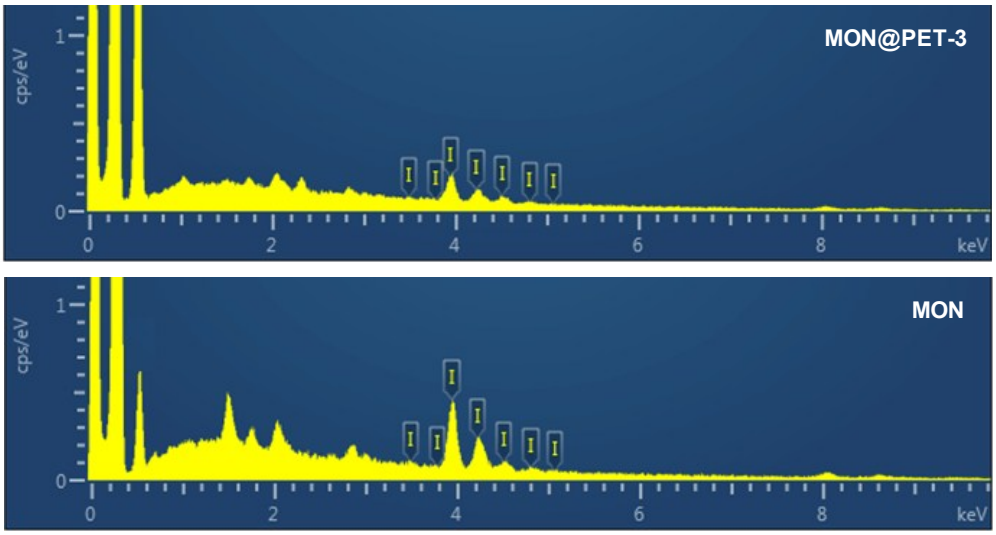



**Fig. S5** UV-vis spectra of mother nitrobenzene solution (3.9 ppm in water) and filtered solution by MON@PET-3 and the activated carbon (Cat#29,259-1 Aldrich Co., 14 mg, same weight of MON@PET-3 with a 1.3 cm diameter) packed on the cotton.

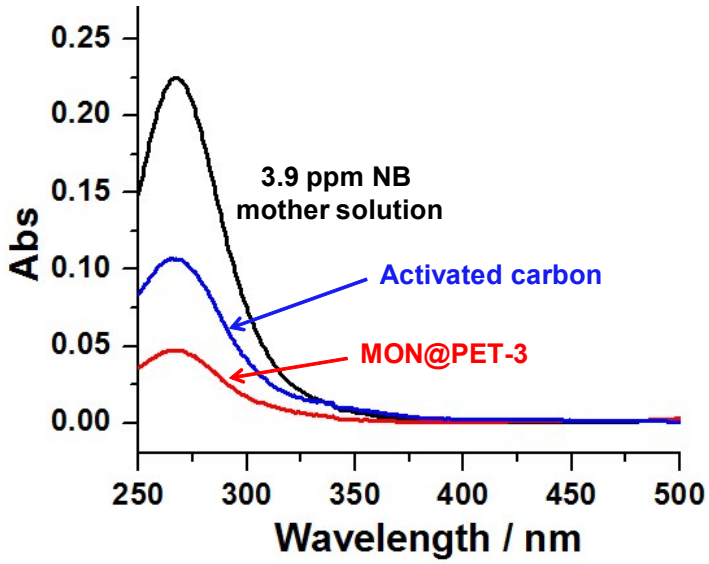


**Table S1.** Elemental analysis of PET, MON@PET-1~5, and MON materials.

| Materials | C /% | H /% | N /% | MON/w%[a] |
|---|---|---|---|---|
| PET | 62.30 | 4.18 | 0.03 | 0 |
| MON@PET-1 | 62.61 | 4.26 | 0.12 | 2.0 |
| MON@PET-2 | 62.74 | 4.70 | 0.12 | 2.9 |
| MON@PET-3 | 62.87 | 4.27 | 0.11 | 3.7 |
| MON@PET-5 | 63.17 | 4.27 | 0.13 | 5.7 |
| MON | 77.64 | 3.75 | 0.45 | 100 |

[a] The values were calculated based on the (ΔC×100)/(77.64-62.30), ΔC = C/% value - 62.30.