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Supporting Information

Mixed matrix membranes with molecular-interaction-driven tunable free volumes for efficient bio-fuel recovery

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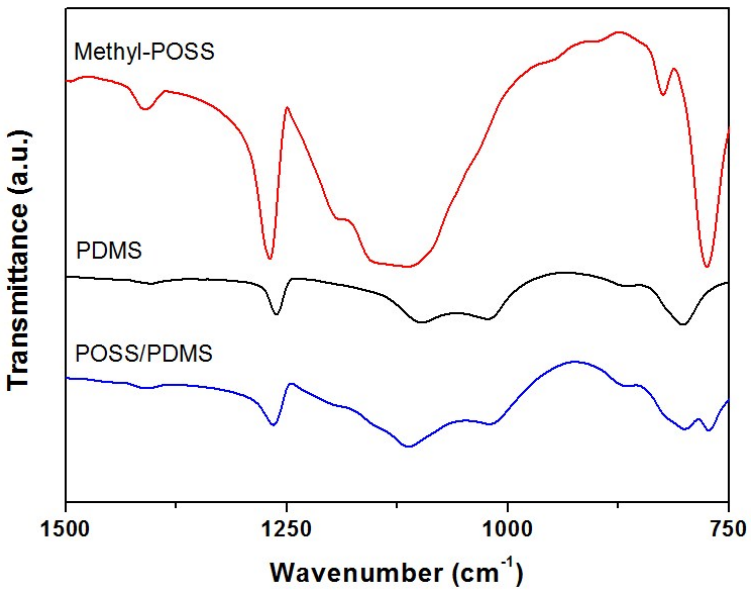

Figure S1. FTIR spectra of POSS particles, PDMS membrane, and POSS/PDMS MMMs

Figure S1 shows that the chemical groups of POSS [$\delta(CH_3)$, ν_{as}(Si-O-Si), ν(Si-C)] also show coincident redshifts in the POSS/PDMS MMMs, as found in the ATR-FTIR analysis.

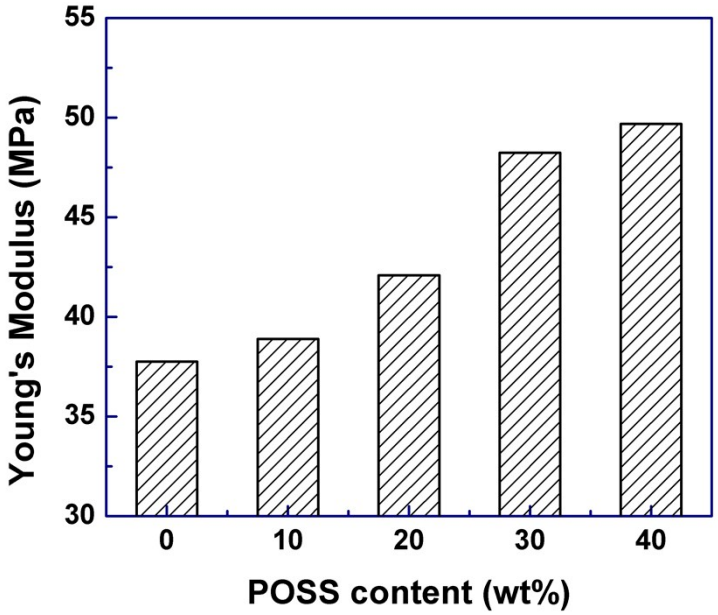

Figure S2. Effect of POSS content on Young's modulus of POSS/PDMS MMMs

Figure S2 shows Young's Modulus of POSS/PDMS MMMs with different POSS content. It is found that the Young's Modulus of the PDMS membrane is greatly increased with the POSS loading.

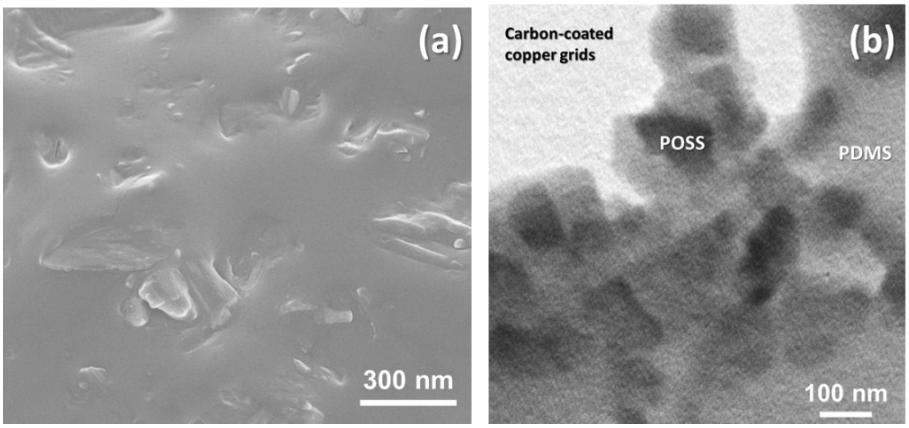

Figure S3. (a) High magnification of cross-sectional SEM image and (b) lower magnification of TEM image of POSS/PDMS membrane (POSS content: 40 wt%)

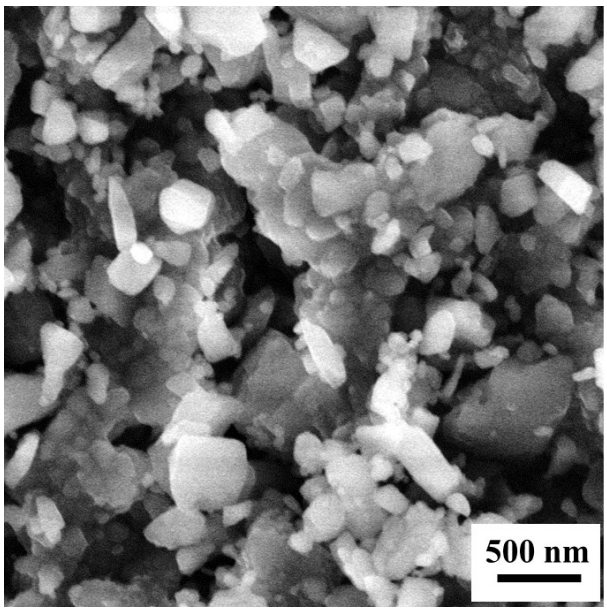

Figure S4. SEM image of POSS particles

As displayed in Figure S4, the size of POSS particles ranges from 100 nm to 500 nm. The POSS fillers with various particle sizes may benefit for construction of hierarchical molecular interactions with polymeric chains.

Table S1 Positron annihilation results for pristine PDMS membranes, POSS/PDMS MMMs, and POSS particles

Sample	τ_3 (ns)	τ_4 (ns)	I_3 (%)	I_4 (%)	R_3 (Å)	R_4 (Å)
PDMS	1.241 ± 0.101	3.135 ± 0.024	10.633 ± 0.976	40.088 ± 1.049	2.020 ± 0.134	3.727 ± 0.011
POSS/PDMS (10 wt%)	1.191 ± 0.053	3.278 ± 0.019	12.851 ± 0.377	38.145 ± 1.865	1.951 ± 0.074	3.819 ± 0.008
POSS/PDMS (20 wt%)	1.149 ± 0.100	3.343 ± 0.030	14.562 ± 0.094	33.949 ± 1.137	1.891 ± 0.144	3.860 ± 0.012
POSS/PDMS (30 wt%)	1.019 ± 0.069	3.385 ± 0.028	18.452 ± 0.211	30.473 ± 1.861	1.692 ± 0.112	3.886 ± 0.011
POSS/PDMS (40 wt%)	1.007 ± 0.047	3.441 ± 0.028	20.227 ± 0.950	27.505 ± 1.949	1.672 ± 0.077	3.921 ± 0.011
POSS	–	2.978 ± 0.083	–	4.991 ± 0.231	–	3.622 ± 0.039

Symbol captions in table: τ_3 and τ_4: *o*-Ps annihilation lifetime; I_3 and I_4:*o*-Ps annihilation lifetime intensity; R_3 and R_4: free-volume hole radius.

Table S1. Comparison of performance of organophilic PV membranes on butanol/water solutions

Membrane	Feed concentration (wt%)	Temp. (ºC)	Total flux (g/m^2h)	Separation factor	Permeate pressure (Pa)	Butanol permeance (10^3 GPU)	Selectivity	Ref.
PERVAP2200	1 [a]	33	330	10	<1000	6.73	2.5	1
PDMS/PE/Brass	1 [a]	37	95	34	<133	3.69	7.1	2
PDMS/PAN	1 [a]	42	1390	22	<100	31	4.1	3
PDMS/ceramic	1 [a]	40	958	18	<300	17.5	3.4	4
PTFE	1 [a]	50	805	10	13300	0.87	0.3	5
PEBA	1 [a]	23	32	12	<665	2.10	4.5	6
PVDF	2.5 [a]	40	990	7.4	<6650	7.49	1.4	7
Ge-ZSM-5	5 [a]	30	20	19	<500	0.63	5.7	8
Silicalite-1/PDMS	1 [a]	40	134	92	66.5-399	2.99	6.4	9
ZIF-8/PMPS	3 [b]	80	8600	35	—	5.78	1.4	10
ZIF-7/PMPS	3 [b]	80	6100	33	—	3.54	1.2	10
ZIF-8/PDMS	1 [a]	80	4846	82	<200	11.1	4.3	11
ZIF-71/PEBA	1 [a]	37	520	19	<400	12.7	4.0	12
POSS/PDMS	1 [a]	40	745	40	<400	24.7	7.4	This work

[a] *n*-butanol/water solution; [b] *i*-butanol/water solution

[c] Because some of the reported membrane thicknesses are unknown, permeance was used for comparison (1 GPU = 1×10^{-6} cm^3 (STP) $cm^{-2}s^{-1}cmHg^{-1}$)

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