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## COMMUNICATION

# Hybrid membranes of metal-organic molecule nanocages for aromatic/aliphatic hydrocarbon separation by pervaporation†

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**Hybrid membranes composed of porous metal-organic molecule nanocages as fillers embedded in hyperbranched polymer (Boltorn W3000) were fabricated, which exhibit excellent pervaporation separation performances towards aromatic/aliphatic hydrocarbons. The unique nature of the molecule-based fillers and their good dispersion and compatibility in/with the polymer are responsible for the good membrane properties.**

The development of efficient and economic technology to separate aromatic hydrocarbons from their aliphatic mixtures has been of great concerns in chemical industry.<sup>1</sup> Usually used techniques in this respect include azeotropic distillation, extractive distillation, liquid-liquid extraction, and membrane separation.<sup>1,2</sup> Among them, the membrane separation has been recognized as one of the most promising approaches, due to its high efficiency, low energy consumption and pollution, and simple manipulation process. Where, the pervaporation (PV), as a popular membrane process is attracting intense interest in the separation of aromatic/aliphatic hydrocarbons.<sup>1,3</sup> The challenge for this technique, like all membrane techniques, is the selection or preparation of high quality membrane with good selectivity and permeability.

Organic-inorganic hybrid membranes, combining advantages of both organic polymer matrix and inorganic particles (such as zeolites,<sup>4a,4b</sup> carbon nanotubes,<sup>4c</sup> silanes,<sup>4d</sup> carbon molecular sieves,<sup>4e</sup> graphene oxide,<sup>4f</sup> and metal-organic frameworks<sup>5</sup>), have been used in the PV membrane separations. Besides their respective inherent natures, the separation performances of this type of membranes mostly lie on the synergistic effect between the polymer and the inorganic particles.<sup>6</sup> Where, a good dispersion and compatibility is crucial. In order to address this issue, some methods for fabricating hybrid membranes have been developed, such as co-blending,<sup>4,5b-5d</sup>

simultaneous spray co-blending,<sup>5a</sup> and coordination driven *in-situ* self-assembly.<sup>7</sup> In these methods, the co-blending is much more popularly adopted than others. In a typical co-blending process, inorganic particles are firstly dispersed in solvent to form suspension, and then mixed with the polymer. Clearly, it is difficult to achieve a high loading of the insoluble inorganic particles while preventing their aggregation.<sup>8</sup> On the other hand, the uniformity in size and surface properties of the inorganic particles has also a significant effect on membrane performances, again being challenged in control.

In order to solve the dispersion and uniformity problems, and at the same time to efficaciously control their loading in polymer, our strategy is to use soluble molecules as fillers to prepare hybrid membranes. Recently, a new type of porous materials, metal-organic polyhedra (MOPs) nanocages emerged, which are discrete molecules being composed of metal ions and organic linkers.<sup>9</sup> Our and others' works have shown that through introducing functional groups into organic ligands, MOPs can become soluble and functionalized.<sup>10</sup> These new porous materials are thus quite promising in the fabrication of hybrid membranes, acting as fillers. However, related studies are lacking, with only one example being documented.<sup>13</sup> In this work, such a membrane with soluble MOP, [Cu<sub>24</sub>(5-*t*Bu-1,3-BDC)<sub>24</sub>(S)<sub>24</sub>] (MOP-*t*Bu, Scheme 1)<sup>12</sup> as fillers was fabricated and firstly used in the PV separation of aromatic/aliphatic hydrocarbons.

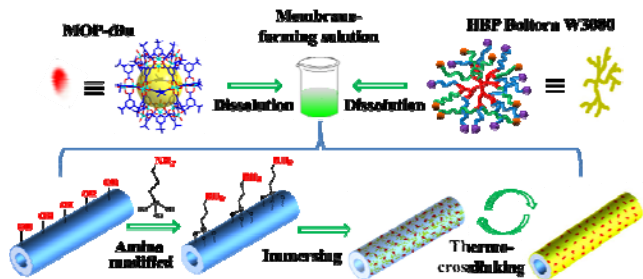
Besides solubility, the MOP-*t*Bu nanocage was selected in view of its open Cu<sup>2+</sup> unsaturated sites (CUSs) and rich benzene rings in its structure, which could endow with good compatibility with the polymer matrix, and high selectivity towards the aromatic compounds.<sup>13</sup> In addition, the MOP-*t*Bu has a large cavity of 16 Å, and two types of small apertures about 4.5 Å and 6.2 Å, respectively.<sup>12</sup> These pores are large enough to allow the as-separated molecules enter into the molecule cavities, which would help to enhance their permeability.

On the other hand, the selection of the polymer matrix is also crucial. Here, we selected hyperbranched polymer Boltorn W3000 due to its superior structure and property.<sup>14</sup> As shown in Scheme 1, W3000 is a macromolecule containing hyperbranched polyester as the core, which is grafted by large number of terminal functional groups, such as hydrophobic fatty acid and hydrophilic polyethylene glycol. These polar groups have a good affinity towards aromatic molecules.<sup>4c,13c,d</sup>

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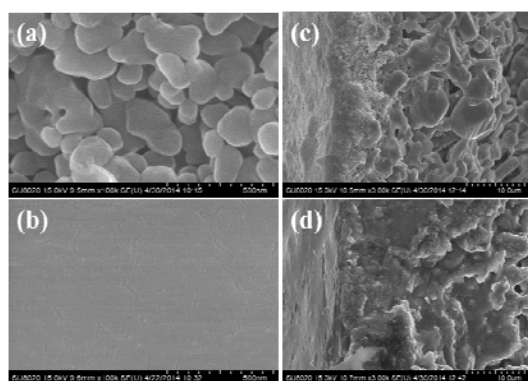
The hybrid tubular membrane was thus fabricated by a simple immerse-coating method as illustrated in Scheme 1. W3000 and MOP-*t*Bu were first dissolved in N-methyl pyrrolidone (NMP) to get membrane-forming solution at room temperature. The MOP-*t*Bu loadings varied from 1.6 to 13.0 wt%. Subsequently, the amino modified ceramic tube was immersed in the solution for 30 min and thermo-crosslinking at 150 °C for 2 h. This immersion and thermo-crosslinking processes were repeated to produce integrated membranes with different layers.



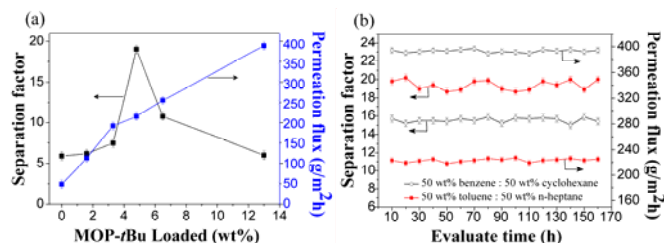
**Scheme 1** Schematic representation of fabricating MOP-*t*Bu/W3000 hybrid membrane on a tubular support.

As shown in Fig. 1 and Fig. S2 (ESI<sup>†</sup>), compared with the bare Al<sub>2</sub>O<sub>3</sub> substrate, the scanning electron microscopy (SEM) images clearly indicate that high quality hybrid membranes were fabricated. More importantly, no particle was found on the surface of the membrane, implying a good dispersion of MOP-*t*Bu molecules in the polymer. From the cross section images it can be seen that the hybrid membrane layer and the sublayer of the Al<sub>2</sub>O<sub>3</sub> substrate indeed match well with each other. Meanwhile, X-ray photoelectron spectroscopy (XPS) shows no Al on the membrane surface and even in depth of approximately 30 nm, which further confirms the formation of a dense hybrid membrane layer on the substrate (Fig. S3 and S4, ESI<sup>†</sup>). But, the presence of Cu in the hybrid layer is confirmed by the XPS, demonstrating the existence of the MOP-*t*Bu (Fig. S3-S5, ESI<sup>†</sup>). In addition, the FTIR spectra also confirm the MOP-*t*Bu in the membrane (Fig. S10, ESI<sup>†</sup>), and the thermal gravimetric analysis shows a high thermal stability up to 300 °C of the prepared membrane (Fig. S11, ESI<sup>†</sup>).

The PV was carried out for the recovery of toluene from its 50 wt% *n*-heptane solution using the fabricated membrane. Effects



**Fig. 1.** SEM images of (a) surface of Al<sub>2</sub>O<sub>3</sub> substrate (100 k), (b) surface of Al<sub>2</sub>O<sub>3</sub>/MOP-*t*Bu/W3000 membrane (100 k) (4.8 wt% MOP-*t*Bu loading, 15 wt% concentration of W3000, two layers), (c) cross-section of Al<sub>2</sub>O<sub>3</sub> substrate (3 k), and (d) cross-section of Al<sub>2</sub>O<sub>3</sub>/MOP-*t*Bu/W3000 membrane (3 k) (4.8 wt% MOP-*t*Bu loading, 15 wt% concentration of W3000, two layers).



**Fig. 2.** (a) Effect of MOP-*t*Bu loading on the performances of the MOP-*t*Bu/W3000 membrane in the separation of 1:1 toluene/*n*-heptane mixture at 40 °C. (b) The stability check of the MOP-*t*Bu/W3000 membrane in the separation of 1:1 toluene/*n*-heptane mixtures and 1:1 benzene/cyclohexane mixture at 40 °C, respectively.

of membrane fabricating and testing conditions on the separation performances were checked. It was found that the thermal cross-linking temperature of the W3000 membrane has an important effect on the PV performances (Fig. S12, ESI<sup>†</sup>). With increasing the temperature, the separation factor increased and the permeate flux decreased, following the “trade off” law. But when the temperature reached 150 °C, the permeate flux and separation factor got a better balance. It was also found that W3000 concentrations affect membrane separation performances. As shown in Fig. S13 (ESI<sup>†</sup>), when the W3000 concentration increased from 5 to 20 wt%, the separation factor of the membrane continuously increased to 6.75, but the flux decreased from 278.5 to 30.7 g/m<sup>2</sup>h. At a 15 wt% concentration of W3000, the resulting membrane shows a good performance with a separation factor of 5.9 and a permeate flux of 50 g/m<sup>2</sup>h.

In addition, the membrane layers and MOP-*t*Bu contents in the hybrid membrane have also important influences on the separation performances. As shown in the Fig. S14 (ESI<sup>†</sup>), with the increase of layer numbers the permeate flux decreased continuously but the separation factor firstly increased and then decreased. The correlation of the PV performances with the MOP-*t*Bu contents in the membrane is shown in Fig. 2a. We can find that the separation factor of the pure W3000 membrane was 5.9 with the permeate flux of 50 g/m<sup>2</sup>h. After the incorporation of MOP-*t*Bu, both permeation flux and separation factor enhanced, up to 220.5 g/m<sup>2</sup>h and 19.0, respectively at a 4.8 wt% MOP loading. After that, the separation factor decreased but the flux continuously increased with the increase of the MOP-*t*Bu loading. This phenomenon could be explained as that the excess MOP-*t*Bu loading reduced the integrality of the hybrid membrane, in which tiny defects might form between organic and inorganic components.

On the other hand, the PV performances of the hybrid membrane are also relative with the feed temperature. It was found that with increasing feed temperature, the separation factor gradually declined but the permeate flux increased continuously, suggesting a reasonable feed temperature of 40 °C (Fig. S15, ESI<sup>†</sup>).

Based on above results, an optimized experimental condition is addressed as: W3000 concentration and MOP-*t*Bu loading should be maintained at 15 wt% and 4.8 wt%, respectively; the thermal cross-linking temperature and feed temperature should be at 150 and 40 °C, respectively; two separation layers of the membrane are better. Under these conditions, such a MOP-based membrane shows excellent PV performances towards the toluene/*n*-heptane separation, giving a permeate flux of 220.5 g/m<sup>2</sup>h and separation factor of 19.0 for a 1:1 mixture. Compared with other reported membranes, this membrane is fairly competitive in the toluene/*n*-heptane separation (see Table S1 in ESI<sup>†</sup>). However, a direct

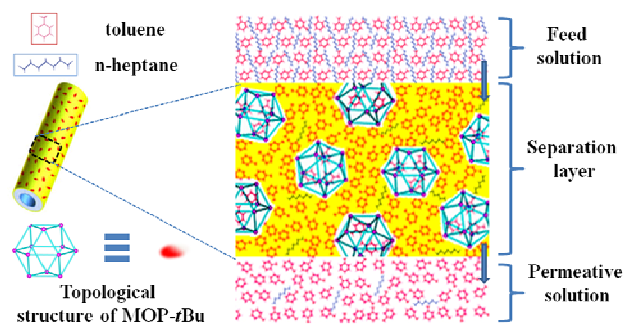


Fig. 3. Proposed transport process of permeating components in the separation layer of the MOP-tBu/W3000 hybrid membrane.

quantitative comparison is limited due to different operation conditions in different membrane/separation systems. This membrane was also evaluated within a relatively wide range of toluene contents in the feed solution. As can be seen from Fig. S16 (ESI<sup>†</sup>), the flux increased continuously, while the separation factor slightly decreased when the toluene contents increased.

Besides, this MOP hybrid membrane also shows a good ability for the enrichment of benzene from 50 wt% benzene/cyclohexane mixture by the PV separation. Under optimized conditions, it can get a permeate flux of 392.3 g/m<sup>2</sup>·h and a separation factor of 15.4 towards benzene, being comparable to some reported membranes (see Table S2 in ESI<sup>†</sup>).

The stability check of the MOP-based hybrid membrane in the separation of toluene/n-heptane and benzene/cyclohexane mixtures was finally performed, respectively. As shown in Fig. 2b, the separation performances of the membrane basically keep at a constant level in a 160 h period of PV process at 40 °C, implying a good stability of the membrane.

We propose that the structural features and compositions of the MOP-tBu might help to improve the transport capabilities and selectivity of the hybrid membrane towards aromatic hydrocarbons (Fig. 3). Firstly, based on the solution-diffusion mechanism, adding MOP-tBu into the W3000 could create more preferential pathways for the aromatic toluene molecules passing, by virtue of their interactions with the CUSs or the  $\pi$ -bond sites of the MOP-tBu. Secondly, because of the high selective adsorption of the toluene on these active sites located near MOP-tBu pore windows, the cavities of MOP-tBu might thus be locked, which restricts the n-heptane molecules entrance, even if n-heptane molecule is smaller than the toluene. As a result, in a given range with the increase of MOP-tBu loading, both the permeate flux and the separation factor increase. Furthermore, the W3000 layer also favors the toluene transport because of its polar groups. Therefore, by combining the advantages of the W3000 and the MOP-tBu, the separation performances of the hybrid membrane have been greatly improved. However, notwithstanding good compatibility between MOP-tBu and W3000, the integrality of the hybrid membrane might decrease with excess MOP-tBu loading, which leads to the lowered separation factor when adding more MOP-tBu.

In summary, we have fabricated high quality PV hybrid membranes with a porous MOP material acting as the inorganic filler. The membranes show excellent performances towards the toluene/n-heptane and benzene/cyclohexane separations. In light of the versatile structures and customizable chemical functionalities of MOPs materials, a lot of this type of hybrid membranes can thus be fabricated for different separation applications, after paving the road in this work.

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### Notes and references

- (a) B. Smitha, D. Suhanya, S. Sridhar, *J. Membr. Sci.*, 2004, **241**, 1; (b) M. T. Ravanchi, T. Kaghazchi and A. Kargari, *Desalination*, 2009, **235**, 199.
- A. Agulyansky, L. Agulyansky and V. F. Travkin, *Chem. Eng. Process*, 2004, **43**, 1231.
- (a) F. Peng, C. Hu and Z. Jiang, *J. Membr. Sci.*, 2007, **297**, 236; (b) S. B. Kuila and S. K. Ray, *Sep. Purif. Technol.*, 2014, **123**, 45.
- (a) S. B. Teli, M. Calle and N. Li, *J. Membr. Sci.*, 2011, **371**, 171; (b) X. Zhang, L. Qian, H. Wang, W. Zhong and Q. Du, *Sep. Purif. Technol.*, 2008, **63**, 434; (c) J.-N. Shen, Y.-X. Chu, H.-M. Ruan, L.-G. Wu, C.-J. Gao and B. V. Bruggen, *J. Membr. Sci.*, 2014, **462**, 160; (d) F. Peng, L. Lu, H. Sun, Y. Wang, J. Liu and Z. Jiang, *Chem. Mater.*, 2005, **17**, 6790; (e) F. Peng, Z. Jiang, C. Hu, Y. Wang, H. Xu and J. Liu, *Sep. Purif. Technol.*, 2006, **48**, 229; (f) N. Wang, S. Ji, J. Li, R. Zhang and G. Zhang, *J. Membr. Sci.*, 2014, **455**, 113.
- (a) H. Fan, Q. Shi, H. Yan, S. Ji, J. Dong and G. Zhang, *Angew. Chem. Int. Ed.*, 2014, **53**, 5578; (b) X.-L. Liu, Y.-S. Li, G.-Q. Zhu, Y.-J. Ban, L.-Y. Xu and W.-S. Yang, *Angew. Chem. Int. Ed.*, 2011, **50**, 10636; (c) J. Yao and H. Wang, *Chem. Soc. Rev.*, 2014, **43**, 4470; (d) D. Hua, Y. K. Ong, Y. Wang, T. Yang and T. S. Chung, *J. Membr. Sci.*, 2014, **453**, 155.
- A. C. Balazs, T. Emrick and T. P. Russell, *Science*, 2006, **314**, 1107.
- R. Zhang, S. Ji, N. Wang, L. Wang, G. Zhang and J.-R. Li, *Angew. Chem. Int. Ed.*, 2014, **53**, 9775.
- (a) T. Yang, G.-M. Shi and T. S. Chung, *Adv. Energy. Mater.*, 2012, **2**, 1358; (b) B. Zornoza, C. Tellez, J. Coronas, J. Gascon and F. Kapteijn, *Micropor. Mesopor. Mat.*, 2013, **166**, 67; (c) J. Campbell, G. Székely, R. P. Davies, D. C. Braddock and A. G. Livingston, *J. Mater. Chem. A*, 2014, **2**, 9260.
- J. J. Perry IV, J. A. Perma and M. J. Zaworotko, *Chem. Soc. Rev.*, 2009, **38**, 1400.
- (a) J.-R. Li, A. Yakovenko, W. Lu, D. J. Timmons, W. Zhuang, D.-Q. Yuan, H.-C. Zhou, *J. Am. Chem. Soc.*, 2010, **132**, 17599; (b) Y. Li, D. Zhang, F. Gai, X. Zhu, Y. Guo, T. Ma, Y. Liu and Q. Huo, *Chem. Commun.*, 2012, **48**, 7946.
- E. V. Perez, K. J. Balkus, J. P. Ferraris and I. H. Musselman, *J. Membr. Sci.*, 2014, **463**, 82.
- J.-R. Li and H.-C. Zhou, *Nat. Chem.*, 2010, **2**, 893.
- (a) M. Rubeš, A. D. Wiersum, P. L. Llewellyn, L. Grajciar, O. Bludský, *J. Phys. Chem. C*, 2013, **117**, 11159; (b) J. Zhang and X. Chen, *J. Am. Chem. Soc.*, 2008, **130**, 6010; (c) F. Sun and E. Ruckenstein, *J. Membr. Sci.*, 1995, **99**, 273; (d) H. H. Schwarz and G. Malsch, *J. Membr. Sci.*, 2005, **247**, 143.
- (a) U. Domańska and Z. Żolek-Tryznowska, *J. Chem. Ther.*, 2010, **42**, 1304; (b) L. Wang, S. Ji, N. Wang, R. Zhang, G. Zhang and J.-R. Li, *J. Membr. Sci.*, 2014, **452**, 143.