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Supporting Information

Embedding Dopamine Nanoaggregates into Poly(dimethylsiloxane) Membrane to Confer Controlled Interactions and Free Volume for Enhanced Separation Performance

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1. TEM analysis of the nanoaggregates

According to **Figure 1**, each type of nanoaggregates (dopamine, dopamine/Cu, dopamine/Ni and dopamine/Ce) exhibited the regularly spherical shape with sizes around 100 nm. From the measurements of particle size distribution analyzer, the sizes of dopamine, dopamine/Cu, dopamine/Ni and dopamine/Ce nanoaggregates were 108, 102, 102 and 74 nm, respectively. The size of dopamine/Ce nanoaggregate was smaller than that of other nanoaggregates. It can be explained that cerium(IV) ammonium nitrate is a superior oxidizing agent under acidic and neutral conditions due to its large reduction potential value of 1.61 V (vs normal hydrogen electrode).[1] Thus, with reducibility surface, the dopamine nanoaggregate was partly oxidized and consumed by the Ce(IV) ion.[2] The dispersion of nanoaggregates was evaluated by polydispersity parameters (*PP*) measured by the particle size distribution analyzer. The dopamine nanoaggregates (*PP*=0.256) tended to agglomerate whereas the dopamine/Cu (*PP*=0.173), dopamine/Ni (*PP*=0.198) and dopamine/Ce (*PP*=0.159) nanoaggregates were evenly dispersed. The metal-organic coordination interaction between transition metal ions and amino- or catechol groups of dopamine/M nanoaggregates was advantageous for suppressing the undesirable agglomeration.

References:

1 V. Nair and A. Deepthi, *Chem. Rev.*, 2007, **107**, 1862.

2 Y. R. Ma, H. Y. Niu, X. L. Zhang and Y. Q. Cai, *Chem. Commun.*, 2011, **47**, 12643.

2. FTIR spectra of the nanoaggregates

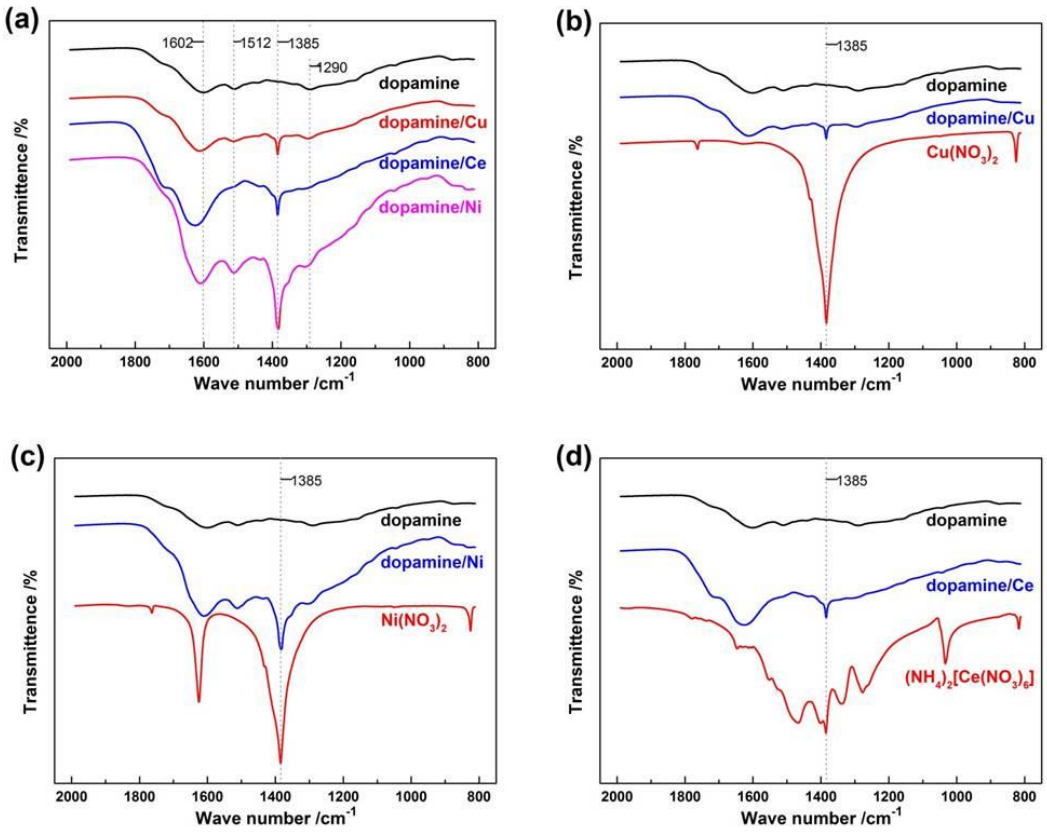

Figure S1. FTIR spectra of **(a)** dopamine, dopamine/Cu, dopamine/Ni and dopamine/Ce nanoaggregates; **(b)** dopamine, dopamine/Cu nanoaggregates and $Cu(NO_3)_2$; **(c)** dopamine, dopamine/Ni nanoaggregates and $Ni(NO_3)_2$; **(d)** dopamine, dopamine/Ce nanoaggregates and $(NH_4)_2[Ce(NO_3)_6]$.

The intensity of band around 1385 cm^{-1} increased when the dopamine nanoaggregate was chelated by the metal ion. This phenomenon reflected the contribution from the nitrate ion adsorbed on the surface of dopamine/M nanoaggregate. The chemical structure of nitrate including $Cu(NO_3)_2$, $Ni(NO_3)_2$, and $(NH_4)_2[Ce(NO_3)_6]$ characterized by FTIR spectra was shown in **Figure S2**. It could be observed that the characteristic peak of nitrate ions in the $Cu(NO_3)_2$, $Ni(NO_3)_2$, and $(NH_4)_2[Ce(NO_3)_6]$ included the absorption bands at 1385 cm^{-1}. The

pristine dopamine nanoaggregate displayed the weak absorption at the same positions, corresponding to N-H bending and aromatic C=N stretching vibration. In contrast, the as-prepared dopamine/M nanoaggregates showed the intense absorption features at around 1385 cm^{-1}, due to the residual nitrate ion on the surface.

3. FTIR spectra of the membranes

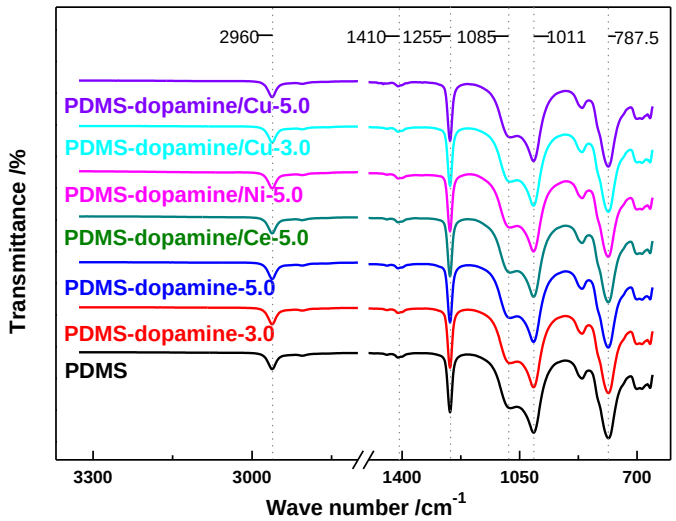

Figure S2. FTIR spectra of the PDMS control, PDMS-dopamine, PDMS-dopamine/Cu, PDMS-dopamine/Ni and PDMS-dopamine/Ce membranes.

The FTIR spectra of the PDMS control, PDMS-dopamine, PDMS-dopamine/Cu, PDMS-dopamine/Ni and PDMS-dopamine/Ce membranes were recorded in **Fig. S2**. The characteristic peak at around 787.5 cm^{-1} in the membranes were assigned to stretching vibrations of Si-C. The peak appeared at about 1085 and 1011 cm^{-1} was corresponded to stretching vibrations of Si-O-Si. The characteristic peak at around 1255 cm^{-1} represented the deformation vibrations of the two methyls linked with Si. The weak absorption peak around 1410 cm^{-1} and 2960 cm^{-1} were the dissymmetry deformation vibrations of methyl joined with Si and stretching vibrations of C-H, respectively. The FTIR spectra of the PDMS-dopamine, PDMS-dopamine/Cu, PDMS-dopamine/Ni and PDMS-dopamine/Ce membranes did not generate new absorption peaks compared with the PDMS control membrane, suggesting that the

nanoaggregates were physically blended within the PDMS matrix.

4. TGA measurements of the nanoaggregates

The TGA of dopamine, dopamine/Cu, dopamine/Ni and dopamine/Ce nanoaggregates was shown in **Figure 5**. The thermal decomposition of dopamine nanoaggregates could be divided into two stages. The first stage indicated a loss of 6.5 wt%, between 40 and 150 ^{o}C, which attributed to the elimination of adsorbed water on the surface of nanoaggregates. The second stage indicated a loss of 48.8 wt%, between 150 and 800 ^{o}C, due to the decomposition of dopamine nanoaggregates. The superior thermal stability of dopamine nanoaggregates ascribed to their inside non-covalent interactions. The thermal decomposition of dopamine/Cu, dopamine/Ni and dopamine/Ce nanoaggregates could be divided into three stages. The first stage of dopamine/M nanoaggregates was attributed to the removing of adsorbed water on the surface. The second stage (110~250 ^{o}C for dopamine/Cu NPs, 140~295 ^{o}C for dopamine/Ni NPs and 125~290 ^{o}C for dopamine/Ce NPs) was attributed to the removal of metallo-chelate on the surface. And the third stage of dopamine/M nanoaggregates was the decomposition of dopamine nanoaggregates.

5. DTA curves of the membranes

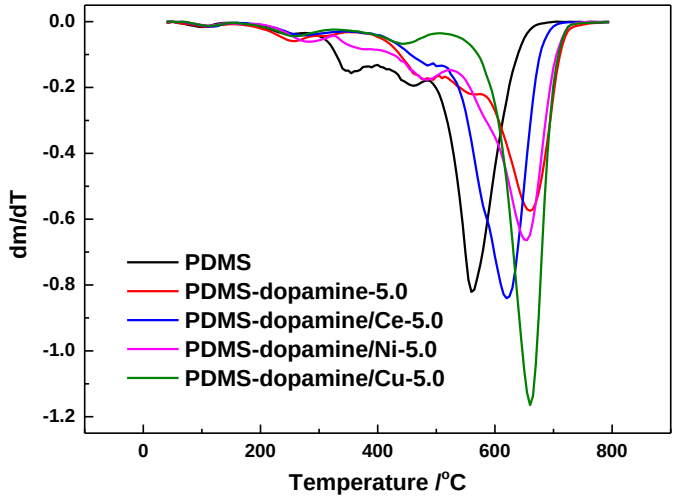

Figure S3. d*m*/d*T* as a function of temperature for the PDMS control, PDMS-dopamine-5.0, PDMS-dopamine/Cu-5.0, PDMS-dopamine/Ni-5.0 and PDMS-dopamine/Ce-5.0 membranes.

6. Effect of the metal ion kinds on membrane separation performance

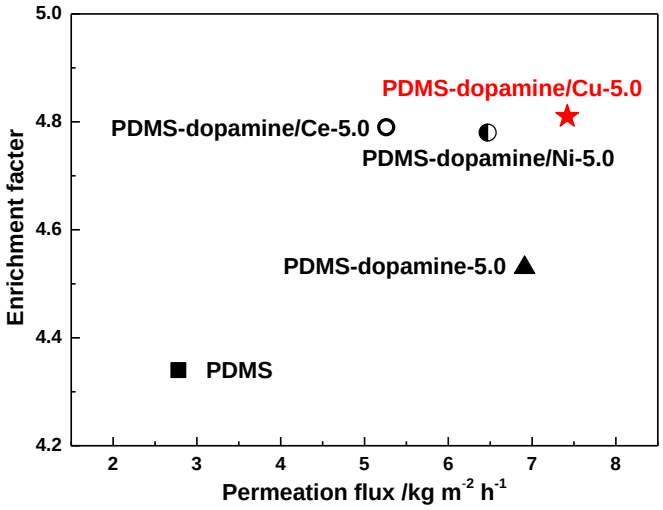

Figure S4. Permeation flux and enrichment factor of PDMS control, PDMS-dopamine-5.0, PDMS-dopamine/Cu-5.0, PDMS-dopamine/Ni-5.0 and PDMS-dopamine/Ce-5.0 membranes for a feed of 1,500 ppmw thiophene in *n*-octane at 303 K with a flow rate of 40 L/h.

7. Arrhenius relationship for permeation of *n*-octane and thiophene through the membranes

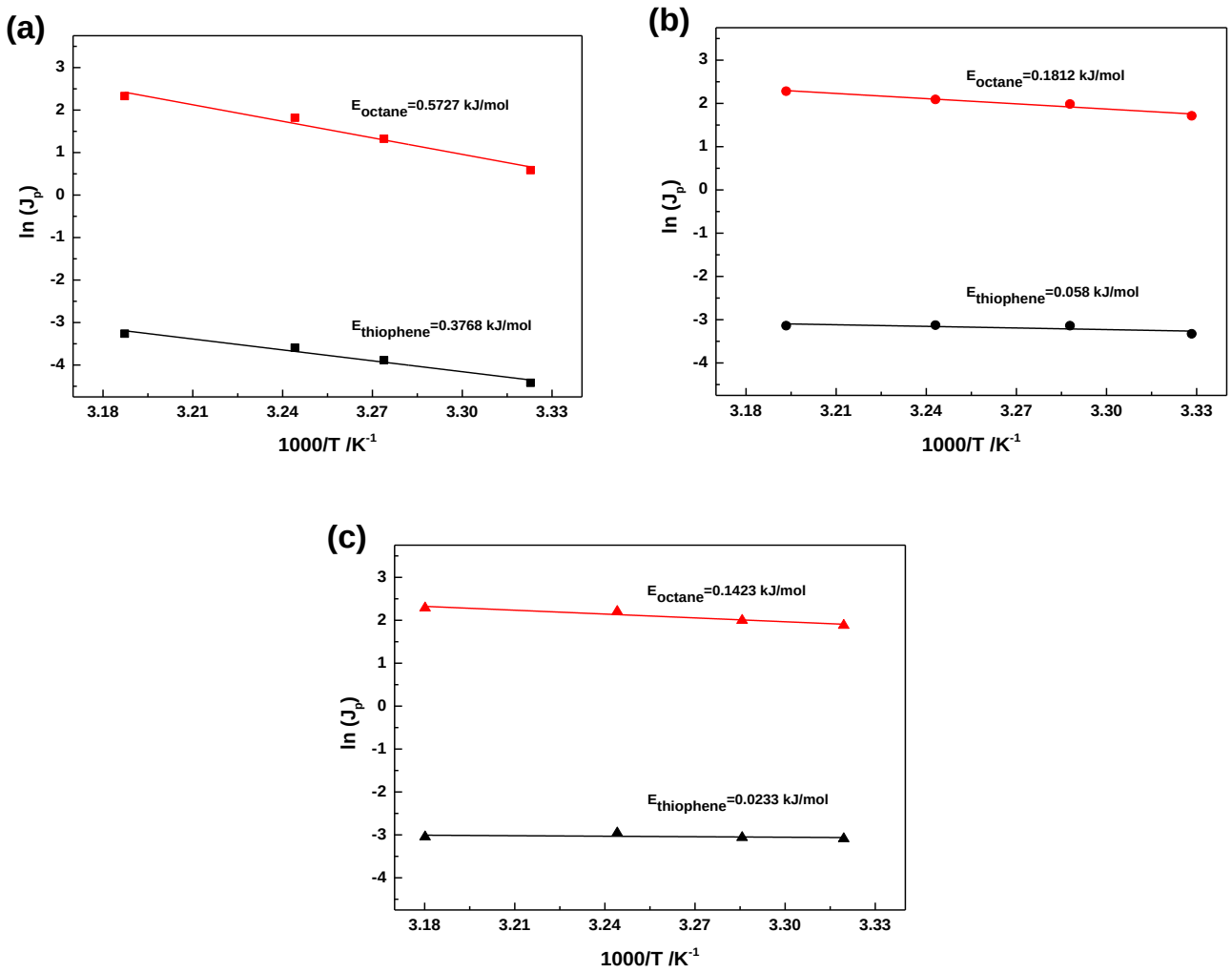

Figure S5. Arrhenius plots of permeation flux for separation of thiophene/octane mixture by **(a)** PDMS control, **(b)** PDMS-dopamine-5.0 and **(c)** PDMS-dopamine/Cu-5.0 membranes for a feed of 1,500 ppmw thiophene in *n*-octane with a flow rate of 40 L/h.

8. Long-term operation stability of the membranes

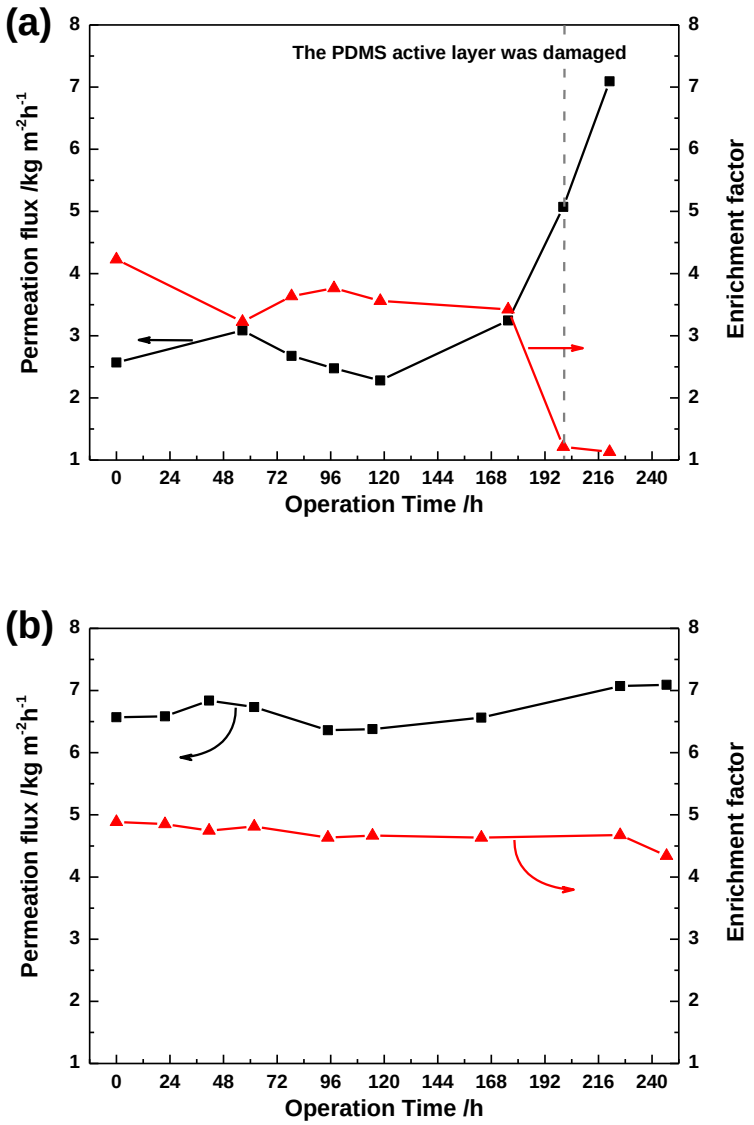

Figure S6. Long-term operation test of **(a)** PDMS control membrane and **(b)** PDMS-dopamine/Cu membrane.

The long-term operation stability is a vital index for the industrial application of membrane. **Figure S6** showed the long-term pervaporation performance test of the PDMS control and PDMS-dopamine/Cu membranes continuously operated for over 250 h for a feed of 1,500 ppmw thiophene in *n*-octane at 303 K with a flow rate of 40 L/h. As shown in **Figure S6(a)**, after 175 h, the active layer of PDMS control

membrane was damaged due to excessive swelling in the penetrant, exhibiting low long-term and chemical stability. During the entire test, the permeation flux and enrichment factor of PDMS-dopamine/Cu membrane remained almost unchanged, as shown in **Figure S6(b)** demonstrating favorable long-term operation stability and implying the desirable structural and chemical stability of as-prepared hybrid membrane.