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Core−Shell Type Ionic Liquid/Metal Organic Framework Composite: An Exceptionally High CO_2/CH_4 Selectivity

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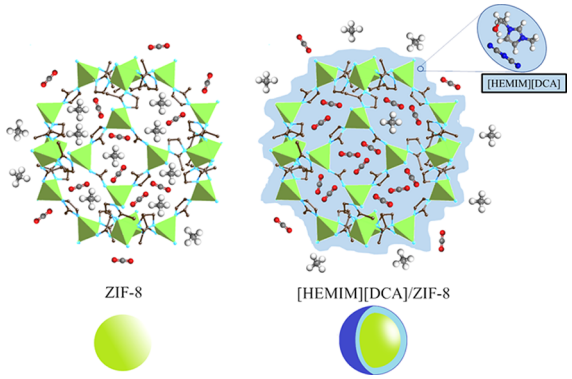
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Supporting Information

ABSTRACT: Here, we present a new concept of a core−shell type ionic liquid/metal organic framework (IL/MOF) composite. A hydrophilic IL, 1-(2-hydroxyethyl)-3-methylimidazolium dicyanamide, [HEMIM][DCA], was deposited on a hydrophobic zeolitic imidazolate framework, ZIF-8. The composite exhibited approximately 5.7 times higher CO_2 uptake and 45 times higher CO_2/CH_4 selectivity at 1 mbar and 25 °C compared to the parent MOF. Characterization showed that IL molecules deposited on the external surface of the MOF, forming a core (MOF)−shell (IL) type material, in which IL acts as a smart gate for the guest molecules.

Metal organic frameworks (MOFs) have been considered as fascinating nanoporous materials for various applications.[1] Among these, CO_2 capture and separation has received tremendous interest.[2] Many MOFs have been synthesized with a wide range of structural and chemical properties; however, the performance of most of them is limited to satisfy the industrial demands for CO_2 separation.[3] Design of MOFs with exceptionally high CO_2 selectivity is a great challenge. An approach to overcome this challenge is to incorporate different chemical components to functionalize MOFs.[4,5] By means of this postsynthesis modification, pore size, pore volume, surface area of MOFs, and the framework-guest interactions can be adjusted to enhance the MOFs' affinity and selectivity toward CO_2. Postsynthesis functionalization of MOFs using alkylamines has been the most successful approach for enhanced CO_2 capture.[6] However, this approach is limited with the types of amines that can be used. A recent more flexible approach is introducing ionic liquids (ILs) into MOFs, referred as "IL incorporation in MOFs" aiming to combine the tunable physicochemical properties of ILs with MOFs.[7] In this approach, accessibility of the adsorption sites is altered accompanied by the creation of new adsorption sites. Here, we introduce another concept on IL/MOF composites. Instead of incorporating the IL into the pores of MOF, we used an IL, 1-(2-hydroxyethyl)-3-methylimidazolium dicyanamide, [HEMIM][DCA], as a shell, covering the external surface of a zeolitic imidazolate framework, ZIF-8. The proposed core−shell type solid IL/MOF composite presented here is illustrated in Scheme 1.

Scheme 1. Proposed Core−Shell Type IL/MOF Structure



The [HEMIM][DCA]/ZIF-8 composite was prepared by wet impregnation at a stoichiometric IL loading of 40 wt%, using acetone as the solvent.[8,9] Following the removal of acetone, the composite in powder form was characterized by combining X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Brunauer−Emmett−Teller (BET) and thermogravimetric analysis (TGA). XRD and SEM results confirmed that the MOF was intact after the deposition of the IL.[10−12] (Figures S1 and S2 in Supporting Information, SI). The FTIR spectra of the IL/MOF composite (Figure S3) illustrated that almost all IR features of [HEMIM][DCA] remained at approximately the same positions in the composite. Figures S4−S6 show that the composite is stable even after washing with water and organic solvents, toluene and pentane.

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Previously, we reported that when both IL and MOF have similar hydrophilicities, the resulting composites show significant changes in the positions of IL's IR features. These changes were attributed to the presence of direct interactions between IL's ions and MOF, indicating incorporation of IL.[8,9] FTIR data complemented by density functional theory (DFT) calculations confirmed the presence of direct electron sharing between the anion of [BMIM][PF_6] and [BMIM][BF_4] and ZIF-8. TGA measurements illustrated that these interactions significantly alter the thermal decomposition mechanism of ILs, reducing the IL's decomposition temperature by more than 50 °C.[8,9] In the present study, the TGA data shown in Figure S7 indicate that the bulk [HEMIM][DCA] starts to decompose at 178 °C, whereas the [HEMIM][DCA]/ZIF-8 composite decomposes at a slightly lower (if not the same within the error range of the measurements) temperature of 171 °C. These results illustrate that the interactions between [HEMIM][DCA] and ZIF-8 are not as strong as those in the previously reported IL-incorporated composites,[8,9,13,14] which is consistent with the FTIR results in Figure S3. Moreover, the BET measurements showed that surface area and pore volume of ZIF-8 decreased significantly from 1208 m^2/g and 0.6332 cm^3/g to 4.53 m^2/g and 0.0015 cm^3/g, respectively, upon the deposition of [HEMIM][DCA]. Accordingly, we inferred that even though the interactions between IL and MOF is not that significant, deposition of IL exposes a direct influence on the accessibility of pores for different guest molecules, hence on the gas separation performances of the MOF as well.

Consistently, Figure 1a,b shows that the presence of IL increases CO_2 uptake of ZIF-8 up to approximately 300 mbar,

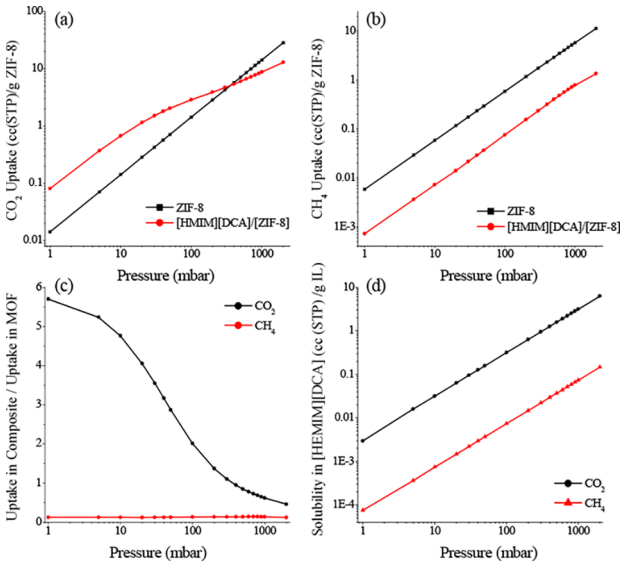


Figure 1. (a) CO_2 (b) CH_4 adsorption isotherm of ZIF-8 and [HEMIM][DCA]/ZIF-8 at room temperature; (c) change in gas adsorptions upon deposition of [HEMIM][DCA]; (d) gas solubility in [HEMIM][DCA] estimated by COSMO-RS calculations.

whereas CH_4 uptake decreases by more than one order of magnitude up to 2000 mbar. Figure 1c shows that CO_2 uptake was approximately 5.7 times of its corresponding value in pristine ZIF-8 at very low pressures (at 1 mbar). Figure S8 confirms the reproducibility of these results. Although some improvements in gas uptakes were previously reported for other IL/MOF composites (Table S1),[8,9] to the best of our knowledge, such an increase in CO_2 uptake on the new [HEMIM][DCA]/ZIF-8 composite that we present here is among the premiers. Because the increase in CO_2 uptake is accompanied by a significant decrease in CH_4 uptake, the new composite, [HEMIM][DCA]/ZIF-8, offers a strong potential for the separation of these two gases.

The ideal CO_2/CH_4 selectivity of the composite was calculated by dividing the gas uptake values obtained from the adsorption isotherms measured up to 2000 mbar. Figure 2

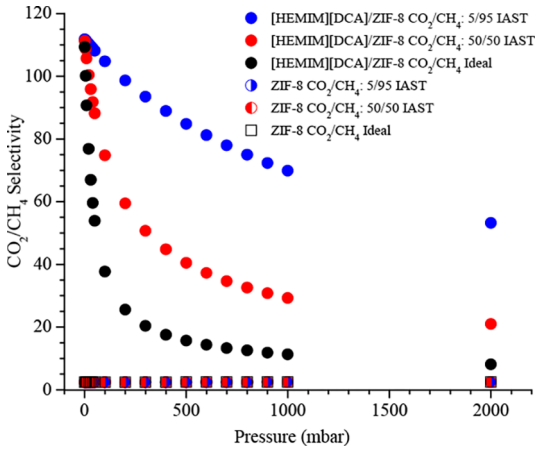


Figure 2. Ideal adsorption selectivity and IAST-predicted selectivities of ZIF-8 and [HEMIM][DCA]/ZIF-8 composite at room temperature.

shows that ideal CO_2/CH_4 selectivity was higher than 110 at 1 mbar and it gradually decreased to approximately 11 when the pressure was increased to 1000 mbar. The corresponding selectivities of the pristine ZIF-8 at these pressures were 2.4 and 2.5, respectively. Figure 2 illustrates that the presence of IL has a positive effect on the ideal selectivity from 1 to 2000 mbar. The effect of IL was significant at very low pressures, at which the improvement in selectivity was by approximately 45 times. Table S1 compares our selectivity results with those obtained on other MOFs prepared by various postsynthesis modification techniques. Accordingly, the highest ideal selectivity previously reported at 1000 mbar and 25 °C for MOF-based functionalized materials (amine-functionalized, ligand/solvent functionalized, and IL-functionalized) was approximately 5.2.[15] In this work, the corresponding ideal selectivity was more than twice of this value under the same conditions, showing the huge potential of the new composite for selective separation of CO_2 from CH_4. Moreover, the comparison presented in Table S2 shows that this selectivity is also superior to the commonly used bulk ILs.

To assess binary gas mixture separation performance of the composite, we fitted the adsorption isotherms (Table S3 and Figure S9) and used ideal adsorbed solution theory (IAST) to predict the selectivity at various compositions.[16] Figure 2 shows that selectivity of the composite was 30 and 70 for separation of CO_2/CH_4 : 50/50 and 5/95 mixtures, respectively, at 1000 mbar and 25 °C. These values compare well with the highest selectivities reported for CO_2/CH_4 mixtures. Zhang et al.[17] reported a selectivity of ~12 for equimolar mixture for a composite prepared by incorporating porphyrin into a MOF, MOM-11. Vahidi et al.[18] grafted piperazine into an amine-functionalized UiO-66 and reported a selectivity of 19 for separation of CO_2/CH_4 : 5/95 mixture.

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Therefore, we inferred that mixture separation performance of our composite is the highest ever reported on a simple postsynthesis functionalized MOF.

This exceptional mixture separation performance is also almost one order of magnitude higher than the results presented in previous reports on IL/MOF composites. In these previous studies, mostly 1,3-dialkylimidazolium type ILs, generally with $[BMIM]^+$ cation, were incorporated into ZIF-8 and characterization confirmed the confinement of IL molecules inside the ZIF cages.[8,9,15,19,20] IL incorporation into the pores became possible because of the flexible pore architecture of ZIF-8 and conformation transition of the 1,3-dialkylimidazolium cations. Furthermore, hydrophobicities of both IL and ZIF-8 were consistent with each other to allow the incorporation of IL into pores. However, the case is not the same in [HEMIM][DCA]/ZIF-8 composite. Though ZIF-8 has a strong hydrophobicity,[21] [HEMIM][DCA] is strongly hydrophilic.[22−24] This difference might be playing a role in preventing ILs to enter into the flexible pore openings.

To investigate whether the IL was mainly deposited on the external surface of ZIF-8 or not, samples were washed with dimethylformamide (DMF), a solvent with a sufficiently large size (5.5 Å)[25] that cannot fit into the pore openings of the ZIF-8 (3.4 Å).[21] According to the FTIR data (Figure S10), after washing [HEMIM][DCA]/ZIF-8 composite with DMF at 50 °C, IL features became very weak, indicating removal of the most of the IL molecules. The filtrate of this washing process indicates the presence of IL molecules (Figure S10c,d). Since DMF is too large to fit into the pores, it can only wash the IL deposited on the external surface of MOF. To further confirm, we applied the same washing process on different IL/MOF composites, $[BMIM][PF_6]$/ZIF-8[8] and [HEMIM][DCA]/CuBTC. These are good examples of internally incorporated IL/MOF composites because of the similar hydrophobicities of the components. Results in Figures S11 and S12 indicate that this washing process cannot remove the internally located IL molecules, supporting our claim that [HEMIM][DCA] molecules were mostly located on the external surface of the ZIF-8. XPS analysis shows an increase in the concentration of nitrogen bonded to the metal node of ZIF-8 accompanied by a decrease in the nitrogen of the IL during the layer-by-layer etching of the sample (Figures S13 and S14). These results further confirm the deposition of [HEMIM][DCA] on the external surface. Additionally, we also obtained direct evidence from TEM. Figure 3 clearly illustrates that IL was externally deposited on the ZIF-8. Images indicate that thickness of the IL shell layer ranges from a few nanometers on isolated particles to approximately 32 nm on the aggregated ZIF-8 particles as illustrated in Figure 3. This varying thickness indicates that composite is not a perfectly organized core−shell material; however, it still presents a core−shell type structure, where the IL is externally deposited on ZIF-8.

Here, the presence of [HEMIM][DCA] layer offers a control over which gas can enter into the pores of ZIF-8. To investigate the influence of [HEMIM][DCA] on the CO_2/CH_4 selectivity of the composite, we performed the Conductor-like Screening Model for Realistic Solvents (COSMO-RS)[26,27] calculations at 25 °C for CO_2 and CH_4 in [HEMIM][DCA]. Figure 1d illustrates that CH_4 is poorly soluble in [HEMIM][DCA], whereas CO_2 has more than one order of magnitude higher solubility. This difference in solubilities describes the exceptional performance of the [HEMIM][DCA]/ZIF-8 composite for CO_2/CH_4 separation.

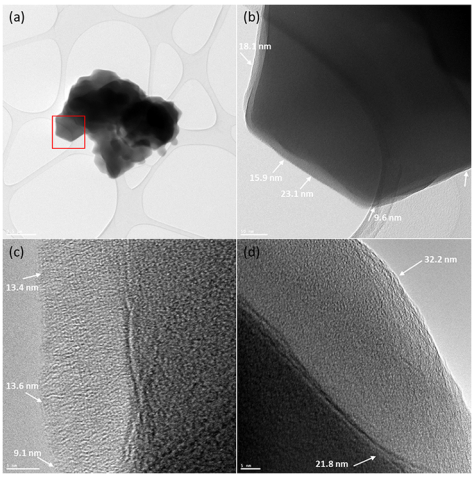


Figure 3. TEM images of [HEMIM][DCA]/ZIF-8 composite. Region in red-box in panel a is magnified in panel b. Panels c and d present higher magnification images at different locations focusing the IL shell, where numbers on images represent the corresponding IL shell thickness at that location.

Apparently, CO_2 can enter into the pores, whereas CH_4 is rejected because of its poor solubility in the IL layer. We envision that [HEMIM][DCA]/ZIF-8 composite presents a new concept of a core−shell type IL/MOF material, where the MOF constituents the core, while the IL covering the external surface as the shell. In this new concept, the IL-shell layer works as a smart gate controlling which gas molecules can enter into the pores.

Such core−shell type IL/MOF composite can offer opportunities to overcome the challenges of previously reported IL-incorporated MOF composites.[8,9,19,20] Even though the presence of IL inside the MOF cages improves the selectivity of MOF for different gas separations, this improvement was limited because the IL occupies a significant portion of the pore space. However, when the IL is deposited on the external surface of ZIF-8, as shown in this work, pore space of MOF is still available for gas adsorption, indicating the superiority of the core−shell type IL/MOF composites for gas separation processes.

To summarize, we report a new core−shell type IL/MOF composite, where the IL, deposited on the external surface of the MOF, controls the selective transport of guest molecules. This new concept provides the highest-level of improvement in CO_2/CH_4 selectivity of a parent MOF by a simple postsynthesis modification. Considering the existence of a large number of IL/MOF pairs suitable for this concept (with opposite hydrophilic characters), the core−shell type IL/MOF composites introduced here will serve as a new platform for high-performance gas separation applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b05802.

Materials, preparation, characterization of samples, gas adsorption results, selectivity comparison of different postsynthesis modified MOFs, XPS and IR data (PDF).

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Zhou, H. C.; Long, J. R.; Yaghi, O. M. *Chem. Rev.* **2012**, *112* (2), 673−674.
(2) Wang, C.; Liu, D.; Lin, W. *J. Am. Chem. Soc.* **2013**, *135* (36), 13222−13234.
(3) Qiao, Z.; Wang, N.; Jiang, J.; Zhou, J. *Chem. Commun.* **2016**, *52* (5), 974−977.
(4) Cohen, S. M. *J. Am. Chem. Soc.* **2017**, *139* (8), 2855−2863.
(5) Von Zons, T.; Brokmann, L.; Lippke, J.; Preuße, T.; Hulsmann, M.; Schaate, A.; Behrens, P.; Godt, A. *Inorg. Chem.* **2018**, *57* (6), 3348−3359.
(6) Flaig, R. W.; Osborn Popp, T. M.; Fracaroli, A. M.; Kapustin, E. A.; Kalmutzki, M. J.; Altamimi, R. M.; Fathieh, F.; Reimer, J. A.; Yaghi, O. M. *J. Am. Chem. Soc.* **2017**, *139*, 12125−12128.
(7) Kinik, F. P.; Uzun, A.; Keskin, S. *ChemSusChem* **2017**, *10* (14), 2842−2863.
(8) Kinik, F. P.; Altintas, C.; Balci, V.; Koyuturk, B.; Uzun, A.; Keskin, S. *ACS Appl. Mater. Interfaces* **2016**, *8* (45), 30992−31005.
(9) Koyuturk, B.; Altintas, C.; Kinik, F. P.; Keskin, S.; Uzun, A. *J. Phys. Chem. C* **2017**, *121* (19), 10370−10381.
(10) Yaghi, O. M.; Hayashi, H.; Banerjee, R.; Park, K. S.; Wang, B. C. Preparation of Functionalized Zeolitic Frameworks. U.S. Patent 8,314,245, 2011.
(11) Schejn, A.; Aboulaich, A.; Balan, L.; Falk, V.; Lalevée, J.; Medjahdi, G.; Aranda, L.; Mozet, K.; Schneider, R. *Catal. Sci. Technol.* **2015**, *5* (3), 1829−1839.
(12) Jian, M.; Liu, B.; Liu, R.; Qu, J.; Wang, H.; Zhang, X. *RSC Adv.* **2015**, *5* (60), 48433−48441.
(13) Singh, M. P.; Dhumal, N. R.; Kim, H. J.; Kiefer, J.; Anderson, J. A. *J. Phys. Chem. C* **2017**, *121* (19), 10577−10586.
(14) Zhang, S.; Zhang, J.; Zhang, Y.; Deng, Y. *Chem. Rev.* **2017**, *117* (10), 6755−6833.
(15) Sezginel, K. B.; Keskin, S.; Uzun, A. *Langmuir* **2016**, *32* (4), 1139−1147.
(16) Lee, S.; Lee, J. H.; Kim, J. *Korean J. Chem. Eng.* **2018**, *35* (1), 214−221.
(17) Zhang, Z.; Gao, W. Y.; Wojtas, L.; Ma, S.; Eddaoudi, M.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2012**, *51* (37), 9330−9334.
(18) Vahidi, M.; Rashidi, A. M.; Tavasoli, A. *J. Iran. Chem. Soc.* **2017**, *14* (10), 2247−2253.
(19) Mohamedali, M.; Ibrahim, H.; Henni, A. *Chem. Eng. J.* **2018**, *334*, 817−828.
(20) Ban, Y.; Li, Z.; Li, Y.; Peng, Y.; Jin, H.; Jiao, W.; Guo, A.; Wang, P.; Yang, Q.; Zhong, C.; Yang, W. *Angew. Chem., Int. Ed.* **2015**, *54* (51), 15483−15487.
(21) Zhang, K.; Lively, R. P.; Zhang, C.; Chance, R. R.; Koros, W. J.; Sholl, D. S.; Nair, S. *J. Phys. Chem. Lett.* **2013**, *4* (21), 3618−3622.
(22) Tsunashima, K.; Kodama, S.; Sugiya, M.; Kunugi, Y. *Electrochim. Acta* **2010**, *56* (2), 762−766.
(23) MacFarlane, D. R.; Golding, J.; Forsyth, S.; Forsyth, M.; Deacon, G. B. *Chem. Commun.* **2001**, *16*, 1430−1431.
(24) MacFarlane, D. R.; Forsyth, S. A.; Golding, J.; Deacon, G. B. *Green Chem.* **2002**, *4* (5), 444−448.
(25) ten Elshof, J. E.; Abadal, C. R.; Sekulić, J.; Chowdhury, S. R.; Blank, D. H. A. *Microporous Mesoporous Mater.* **2003**, *65* (2−3), 197−208.
(26) Palomar, J.; Ferro, V. R.; Torrecilla, J. S.; Rodriguez, F. *Ind. Eng. Chem. Res.* **2007**, *46* (18), 6041−6048.
(27) Anantharaj, R.; Banerjee, T. *Ind. Eng. Chem. Res.* **2010**, *49* (18), 8705−8725.

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