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Shang, Shanshan; Yang, Chao; Wang, Chenguang; Qin, Junsheng; Li, Yi; Gu, Qinfen; Shang, Jin

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Transition Metal Inserted Porphyrin Metal-Organic Frameworks as π -backbonding Adsorbents for NO₂ Removal

Shanshan Shang,^[a] Chao Yang,^[b] Chenguang Wang,^[c] Junsheng Qin,^[d] Yi Li,^[d] Qinfen Gu*,^[e] and Jin

Shang*^[a]

- [a] S. Shang, Dr. J. Shang
School of Energy and Environment
City University of Hong Kong
Tat Chee Avenue, Kowloon, Hong Kong, P.R. China
E-mail: jinshang@cityu.edu.hk
- [b] C. Yang
Department of Civil Engineering
The University of Hong Kong
Pokfulam, Hong Kong, P.R. China
- [c] Prof. Dr. C. Wang
Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion,
Chinese Academy of Sciences
Guangzhou 510640, P. R. China
- [d] Prof. Dr. J. Qin, Prof. Dr. Y. Li
State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry,
Jilin University
2699 Qianjin Street, Changchun 130012, P. R. China
- [e] Dr. Q. Gu
Australian Synchrotron, ANSTO
800 Blackburn Rd, Clayton, Victoria 3168, Australia.
E-mail: qinfeng@ansto.gov.au

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Abstract: Mitigating ambient nitrogen dioxide (NO₂) pollution via selective adsorption on porous materials represents a promising approach to tackle such an increasingly pressing environmental health issue. However, very few porous adsorbents have sufficiently high NO₂ adsorption capacity and good regenerability simultaneously. Here we attempt to address this challenge by developing π -backbonding adsorbents in the transition metal (TM) incorporated porphyrin metal-organic frameworks (PMOFs). Breakthrough experiments show that PMOFs with inserted TMs achieve appreciable NO₂ capacity and good regenerability. Combined *in-situ* DRIFTS, synchrotron powder XRD, and DFT calculations reveal the adsorption mechanism – NO₂ partially transforms to N₂O₄ and interacts with transition metal via π -backbonding and Al-node via hydrogen bonding. This work affords new insights for designing next-generation adsorbents for ambient NO₂ removal and presents PMOFs as a platform to tailor π -backbonding adsorbents.

Nitrogen dioxide (NO₂) pollution causes serious environmental problems and poses substantial health threats to human beings.^[1] Various NO₂ emission sources, such as exhaust from vehicles, flue gas from burning of fossil fuels, contribute to the accumulation of NO₂ in the atmosphere.^[2] Although the selective catalytic reduction (SCR) applicable for NO₂ conversion at high temperatures (523-873 K) has been widely used in industry,^[3] the control and abatement of ambient NO₂ emission is still an elusive challenge. The development of efficient technologies for ambient NO₂ removal is highly sought-after.

Gas adsorption by solid materials is a cost-effective and promising approach for ambient NO₂ removal.^[4] Given its highly reactive nature, many solid adsorbents are vulnerable to NO₂ and thus very limited studies have been done on silica,^[5] carbon

materials,^[6] zeolites,^[7] and metal-organic frameworks (MOFs) and their composites.^[4, 8] Among them, MOFs are most promising thanks to their tunable porosity and functionality.^[4] Two major adsorption mechanisms for NO₂ removal have been studied on MOFs.^[4, 9] One is the chemical acid-base interaction, which can be achieved by grafting ammine groups to MOFs as active sites for acidic NO₂ molecules.^[8b, 10] The other is the Lewis acid-base interaction, which is generally imparted by open metal sites (OMS) in MOFs. These interactions are always too strong to ensure regenerability and reusability of adsorbents. Achieving high NO₂ capacity and good regenerability requires a moderate interaction between NO₂ and adsorption sites in a stable porous solid.

Designing porous adsorbents with accessible active sites capable of backbonding target molecules is conducive to high adsorption capacity and regenerability toward NO₂. Porphyrin-based metal-organic frameworks (PMOFs) could be a good candidate. Recent years saw the exploration of PMOFs for various applications,^[11] due to their multi-domain functionality, high stability, and high porosity. A unique feature of PMOFs lies in that different transition metals (TMs) can be accommodated in the porphyrin ring to form metalloporphyrin^[12] and impart π -backbonding interactions. The π -backbonding is formed by the backdonation of d orbital electrons of TMs to the π^* orbital of π -acidity adsorbates.^[13] The strength of π -backbonding is between that of physisorption and that of chemisorption, readily allowing for good adsorption capacity and reversibility.^[13] Herein, we report an aluminum-based PMOF (Al-PMOF) as π -backbonding adsorbent, which engages π -acid gas NO₂ via inserted TMs (nickel (Ni^{II}), cobalt (Co^{II}), copper (Cu^{II}) and zinc (Zn^{II})) as active adsorption sites. The moderate interaction of π -backbonding and the ultrastable substrate allow the Al-PMOF(Ni) to exhibit a

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superior NO₂ adsorption capacity and regenerability at ambient conditions, qualifying it as a potential candidate for NO₂ removal.

Al-PMOF-based adsorbents were prepared and characterized to verify our adsorbents design. The parent Al-PMOF was synthesized using a reported hydrothermal method^[11a] with some modifications (see Supporting Information). The insertion of TMs into Al-PMOF was achieved using a post-synthetic method,^[11a, 14] resulting in Al-PMOF(M), i.e., Al-PMOF(Ni), Al-PMOF(Co), Al-PMOF(Cu), and Al-PMOF(Zn) (Figure 1). The successful synthesis of high purity PMOFs was verified by Synchrotron powder X-ray diffraction (PXRD) (Figure 2a,b, Figure S1). The Rietveld refinement shows Al-PMOF has an orthorhombic cell ($a=32.0673$ Å, $b=6.5922$ Å, $c=16.7405$ Å, and $V=3538.9014$ Å³) in the *Cmmm* space group, agreeing with that previously reported^[11a] and the insertion of TMs in the plane of porphyrin ring does not affect the crystallinity and integrity of Al-PMOF. Nitrogen adsorption on PMOFs at 77 K (Figure S2) shows the specific surface area is in the range of 405-458 m² g⁻¹ (Table S1) and pore size distribution of 5-11 Å. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDS) elemental mapping (Figure 2c and Figure S3) of the representative Al-PMOF(Ni) displays nanoplate-like crystals with a thickness of 15-25 nm and a homogeneous dispersion of the incorporated Ni atom, agreeing with those previously reported.^[14a] Solid-state ultraviolet-visible spectroscopy (UV-Vis) further confirms the successful incorporation of TMs into the porphyrin ring. Specifically, the decrease in the numbers of Q bands, from four for Al-PMOF to two for Al-PMOF(Ni) (Figure 2d), suggests an increase in symmetry upon metal insertion.^[14a, 15]

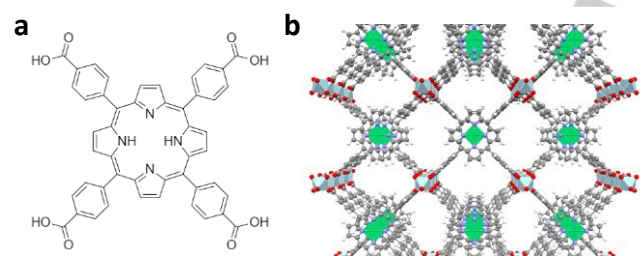


Figure 1. Construction of Al-PMOF(M) a) Views of ligand H₂TCPP and b) Al-PMOF(M) framework structure along the *b* axis. Color scheme: C, grey; N, purple; H, white; O, red; Al, light blue; and Ni, green.

The NO₂ adsorption on PMOF adsorbents was evaluated by dynamic column breakthrough experiments (Figure 3a) at ambient conditions. Figure 3b shows Al-PMOF(Ni) has the highest NO₂ capacity (2.30 mmol/g) among our PMOF adsorbents, reflected by the longest breakthrough time, followed by Al-PMOF(Co), Al-PMOF, Al-PMOF(Cu), and Al-PMOF(Zn) (Figure 3d). This value on Al-PMOF(Ni) is comparable to some representative MOFs, such as UiO-66, UiO-67, and CuBTC (Table S2).^[8c, 16] Importantly, a significant elevation of NO₂ adsorption capacity with respect to the parent Al-PMOF was observed on Al-PMOF(Ni) and Al-PMOF(Co), but not on Al-PMOF(Cu) or Al-PMOF(Zn). This is because the unsaturated Ni and Co sites have higher affinity toward NO₂ compared with Cu and Zn sites in PMOF, as evidenced by the binding energy

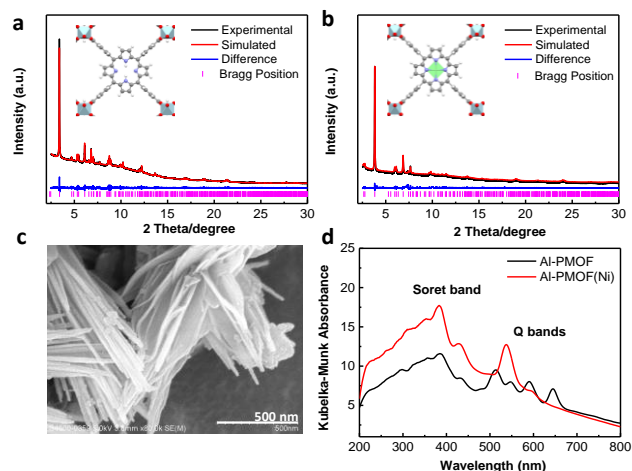


Figure 2. a,b) The synchrotron PXRD patterns of Al-PMOF and Al-PMOF(Ni) with Rietveld refinement. The insets show the crystal structure viewed down [010] direction. c) The SEM image of Al-PMOF(Ni) shows the nanoplate morphology. d) Solid-state UV-Vis spectra of Al-PMOF and Al-PMOF(Ni) prove the insertion of metal into the porphyrin ring.

calculated by Density Functional Theory (DFT). The binding energies of NO₂ on Al-PMOF(Ni) and Al-PMOF(Co) are -0.45 and -0.35 eV, respectively, followed by Al-PMOF (-0.29 eV), Al-PMOF(Zn) (-0.22 eV) and Al-PMOF(Cu) (-0.20 eV). The moderately strong affinity of Ni to NO₂ is also evidenced by the fact that the IR peaks representing adsorbed NO₂ remain upon helium sweeping below 393 K (Figure 4c).

The amount of NO generation upon NO₂ adsorption is important for assessing adsorbents. NO was released upon NO₂ adsorption for all PMOF adsorbents (Figure 3c) due to NO₂ reduction,^[8b] in the range being 19.9-23.5% of the total NO₂ input. Al-PMOF(Ni) shows better NO retention ability than others. A lower ratio of NO generation is desired as NO is also a toxic gas. Our PMOF adsorbents show less NO release proportion than most other reported porous materials, approximate ~30%^[10, 16] and thus desirable.

The regenerability of our PMOF adsorbents is vital for their real-world applications and assessed by cyclic NO₂ adsorption experiments. The NO₂ capacity of Al-PMOF(Ni) maintained above 90% after 3 adsorption-regeneration cycles (Figure S4), indicating the reversible NO₂ adsorption. Note that few MOF adsorbents retain their structure upon NO₂ adsorption, inhibiting cyclic NO₂ adsorption.^[8c, 10] The structural integrity of Al-PMOF(Ni) was maintained as confirmed by the powder XRD patterns (Figure S5), indicating the good material stability upon NO₂ adsorption. The high regenerability was also verified by following *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) (Supporting information) of NO₂ on Al-PMOF(Ni). The peaks representing adsorbed NO₂ and N₂O₄ disappear upon desorption (helium sweeping at 393 K) and reappear upon introducing NO₂ (Figure 4d). Overall, the moderate interaction between the TM and NO₂ enables to achieve good capacity, low NO generation, and excellent regenerability.

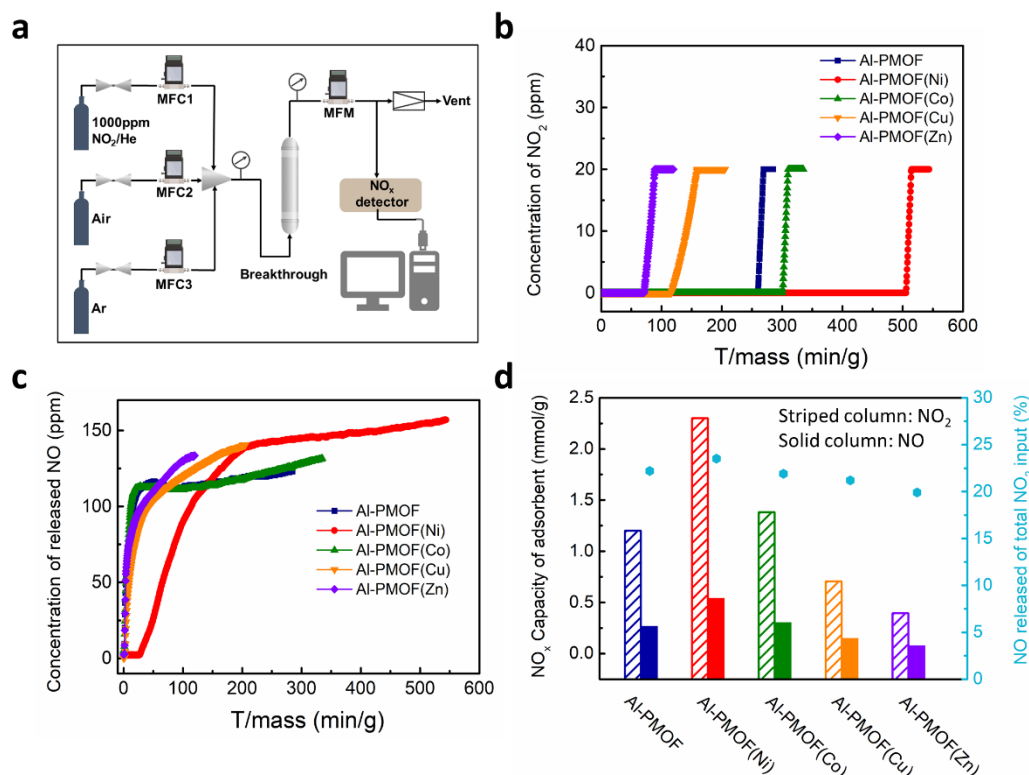


Figure 3. a) The schematic of setup for NO₂ breakthrough experiment. b) NO₂ breakthrough curves. Al-PMOF(Ni) shows the longest breakthrough time (C=20 ppm) and the highest NO₂ adsorption capacity among five PMOF adsorbents. c) NO breakthrough curves. d) The capacity of NO_x, including NO and NO₂, and NO generation of total NO₂ input of Al-PMOF and Al-PMOF(M).

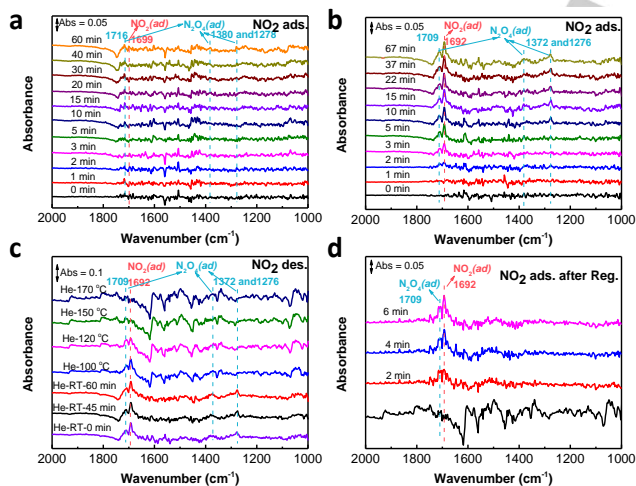


Figure 4. *In-situ* DRIFTS spectra of a) Al-PMOF and b) Al-PMOF(Ni) during NO₂ adsorption. Al-PMOF(Ni) during NO₂ desorption c), and d) NO₂ adsorption after regeneration.

To elucidate the adsorption mechanism, we compare NO₂ adsorption on Al-PMOF and Al-PMOF(Ni) by *in-situ* DRIFTS (Figure 4). The peaks representing N₂O₄ at 1716, 1380, and 1278 cm⁻¹ ($\nu(\text{NO})$)^[17] suggest NO₂ partially transform into N₂O₄ upon adsorption, which was also observed in other MOF, i.e., MFM-300(Al) and MFM-520.^[1, 18] Those peaks representing N₂O₄ and NO₂ (1692 cm⁻¹) in Al-PMOF(Ni) (Figure 4b) undergo a redshift of approximately 7 cm⁻¹ with respect to Al-PMOF (Figure 4a), clearly suggesting π -backbonding between Ni and NO₂, in contrast to the

blueshift observed in the MOFs via Lewis-acidic mechanism.^[13, 19] The depletion of bands representing the hydroxyl (-OH) group at 3708 and 3710 cm⁻¹ (Figure S6), respectively, was ascribed to the formation of hydrogen bonding between the Al-OH metal node and NO₂.

To further establish the adsorption mechanism, we investigated the adsorption of NO₂ at the atomic scale using *in-situ* synchrotron PXRD coupled with DFT calculations. The calculated difference electron density map (Figure S8) from PXRD patterns (Figure S7) of Al-PMOF(Ni) with loaded NO₂ shows that most of the residual electrons are near Ni atoms, suggesting the major adsorption sites are isolated Ni featuring π -backbonding. The side-on (configuration b) and end-on (configuration e) adsorption modes are most probably in the case of Ni insertion (Figure S9), reflected by the highest binding energy (Table S3). The distance (N^{NO₂}-Ni) from Ni(δ^-) center to N(δ^+) of NO₂ is 2.07 Å for the former and the distance (O^{NO₂}-Ni) from Ni(δ^-) center to O(δ^+) of NO₂ is 2.08 Å for the latter (Table S3). The net charge gained by NO₂ upon adsorption (configuration b) is 0.408 e (Figure 5), suggesting the backdonation of electrons from Ni to NO₂. NO₂ gains more electrons from Al-PMOF(Ni) than from Al-PMOF, thus the adsorbed NO₂ bands showing little redshift in the IR spectra. Importantly, this π -backbonding dominated interaction is not excessively strong so that the NO₂ adsorption is readily reversible.

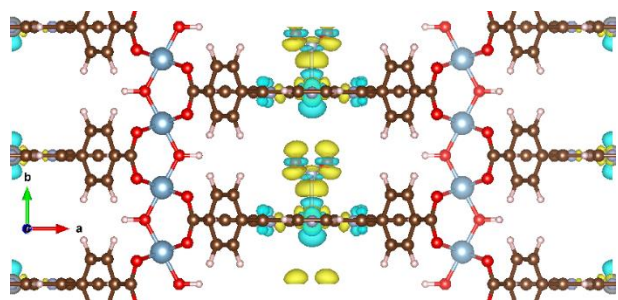


Figure 5. View of charge density difference for Al-PMOF(Ni) loaded with NO₂ with b configuration (yellow: positive density difference; cyan: negative density difference).

Conclusions

The transition metal inserted porphyrin-based metal-organic frameworks demonstrate great potential for NO₂ removal at ambient conditions as platform adsorbents featuring moderate and reversible π -backbonding interaction. The *in-situ* DRIFTS and synchrotron PXRD combined with DFT calculations enable to elucidate the NO₂ adsorption mechanism, π -backbonding and hydrogen bonding between the PMOF adsorbents and NO₂. We contend that altering the type of porphyrin scaffold could be another handle, apart from inserted metal centers, to tune the adsorption properties of PMOF. This study unleashes the potential of π -backbonding as a design principle and affords new insights for developing next-generation adsorbents in wide-range applications.

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Conflict of interest

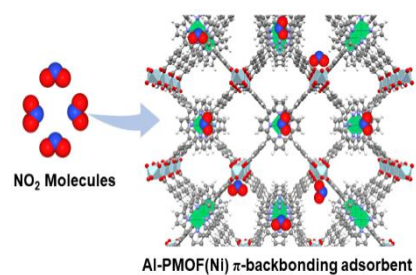
The authors declare no conflict interest.

Keywords: porphyrin metal-organic frameworks • π -backbonding • NO₂ adsorption • Al-PMOF(Ni)

- [1] J. Li, X. Han, X. Zhang, A. M. Sheveleva, Y. Cheng, F. Tuna, E. J. L. McInnes, L. J. McCormick McPherson, S. J. Teat, L. L. Daemen, A. J. Ramirez-Cuesta, M. Schroder, S. Yang, *Nat. Chem.* **2019**, *11*, 1085-1090.
- [2] M. Schulz, A. Gehl, J. Schlenkrich, H. A. Schulze, S. Zimmermann, A. Schaate, *Angew. Chem. Int. Ed.* **2018**, *57*, 12961-12965.
- [3] E. Bello, V. J. Margarit, E. M. Gallego, F. Schuetze, C. Hengst, A. Corma, M. Moliner, *Micropor. Mesopor. Mat.* **2020**, *302*, 110222.
- [4] X. Han, S. Yang, M. Schröder, *Nat. Rev. Chem.* **2019**, *3*, 108-118.
- [5] B. Levasseur, A. M. Ebrahim, T. J. Bandoz, *Langmuir* **2012**, *28*, 5703-5714.

- [6] A. A. Abdulrasheed, A. A. Jalil, S. Triwahyono, M. A. A. Zaini, Y. Gambo, M. Ibrahim, *Renew. Sust. Energ. Rev.* **2018**, *94*, 1067-1085.
- [7] J.F. Brillhac, A. Sultana, P. Gilot, Martens, *Environ. Sci. Technol.* **2002**, *36*, 1136-1140.
- [8] a) S. Bhattacharyya, R. Han, J. N. Joshi, G. Zhu, R. P. Lively, K. S. Walton, D. S. Sholl, S. Nair, *J. Phys. Chem. C* **2019**, *123*, 2336-2346; b) G. W. Peterson, J. J. Mahle, J. B. DeCoste, W. O. Gordon, J. A. Rossin, *Angew. Chem. Int. Ed.* **2016**, *55*, 6235-6238; c) B. Levasseur, C. Petit, T. J. Bandoz, *ACS Appl. Mater. Inter.* **2010**, *2*, 3606-3613.
- [9] I. Ahmed, S. H. Jung, *J. Hazard. Mater.* **2016**, *301*, 259-276.
- [10] A. M. Ebrahim, T. J. Bandoz, *Micropor. Mesopor. Mat.* **2014**, *188*, 149-162.
- [11] a) A. Fateeva, P. A. Chater, C. P. Ireland, A. A. Tahir, Y. Z. Khimyak, P. V. Wiper, J. R. Darwent, M. J. Rosseinsky, *Angew. Chem. Int. Ed.* **2012**, *51*, 7440-7444; b) N. Kornienko, Y. Zhao, C. S. Kley, C. Zhu, D. Kim, S. Lin, C. J. Chang, O. M. Yaghi, P. Yang, *J. Am. Chem. Soc.* **2015**, *137*, 14129-14135; c) T. Wilcox, A. Fateeva, A. P. Katsoulidis, M. W. Smith, C. A. Stone, M. J. Rosseinsky, *Chem. Commun.* **2015**, *51*, 14989-14991.
- [12] L. Feng, K.Y. Wang, E. Joseph, H.C. Zhou, *Trends Chem.* **2020**, *2*, 555-568.
- [13] D. E. Jaramillo, D. A. Reed, H. Z. H. Jiang, J. Oktawiec, M. W. Mara, A. C. Forse, D. J. Lussier, R. A. Murphy, M. Cunningham, V. Colombo, D. K. Shuh, J. A. Reimer, J. R. Long, *Nat. Mater.* **2020**, *19*, 517-521.
- [14] a) Y. Liu, Y. Yang, Q. Sun, Z. Wang, B. Huang, Y. Dai, X. Qin, X. Zhang, *ACS Appl. Mater. Inter.* **2013**, *5*, 7654-7658; b) M. Lions, J. B. Tommasino, R. Chattot, B. Abeykoon, N. Guillou, T. Devic, A. Demessence, L. Cardenas, F. Maillard, A. Fateeva, *Chem. Commun.* **2017**, *53*, 6496-6499.
- [15] B. Abeykoon, T. Devic, J. M. Greneche, A. Fateeva, A. B. Sorokin, *Chem. Commun.* **2018**, *54*, 10308-10311.
- [16] A. M. Ebrahim, B. Levasseur, T. J. Bandoz, *Langmuir* **2013**, *29*, 168-174.
- [17] a) K. Tan, S. Zuluaga, Q. Gong, Y. Gao, N. Nijem, J. Li, T. Thonhauser, Y. J. Chabal, *Chem. Mater.* **2015**, *27*, 2203-2217; b) L. Sivachandiran, F. Thevenet, A. Rousseau, D. Bianchi, *Appl. Catal. B Environ.* **2016**, *198*, 411-419.
- [18] J. W. Yoon, H. Chang, S. J. Lee, Y. K. Hwang, D. Y. Hong, S. K. Lee, J. S. Lee, S. Jang, T. U. Yoon, K. Kwac, Y. Jung, R. S. Pillai, F. Faucher, A. Vimont, M. Daturi, G. Ferey, C. Serre, G. Maurin, Y. S. Bae, J. S. Chang, *Nat. Mater.* **2017**, *16*, 526-531.
- [19] X. Han, H. G. W. Godfrey, L. Briggs, A. J. Davies, Y. Cheng, L. L. Daemen, A. M. Sheveleva, F. Tuna, E. J. L. McInnes, J. Sun, C. Drathen, M. W. George, A. J. Ramirez-Cuesta, K. M. Thomas, S. Yang, M. Schroder, *Nat. Mater.* **2018**, *17*, 691-696.

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A moderate and reversible interaction dominated by the π -backbonding between NO₂ and adsorbent was achieved by insertion of transition metal into porphyrin metal-organic frameworks. The accommodated Ni and Al-OH nodes serve as the active NO₂ adsorption sites.