Regulating C$_2$H$_2$/CO$_2$ adsorption selectivity by electronic-state manipulation of iron in metal-organic frameworks


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Regulating C₂H₂/CO₂ adsorption selectivity by electronic-state manipulation of iron in metal-organic frameworks

Chen et al. report a metal electronic-state manipulation strategy to construct a pair of isostructural and interconvertible Fe-MOFs featuring open Fe centers with different electron densities for efficient C₂H₂/CO₂ separation. They show that the presence of Fe[II] centers with a medium-spin-state trail plays a crucial role in the enhanced C₂H₂ selective adsorption.

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Highlights
The electronic state of Fe can be purposely tuned to regulate C₂H₂/CO₂ separation
Increasing electron density of Fe centers results in enhanced C₂H₂ adsorption
The interconvertible nature deepens understanding of structure-property relationship
Distinct adsorption mechanism is unveiled through in situ FTIR and molecular simulation

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Regulating C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2} adsorption selectivity by electronic-state manipulation of iron in metal-organic frameworks

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SUMMARY
The separation of C\textsubscript{2}H\textsubscript{2} from C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2} mixture is of great importance, yet highly challenging in the petrochemical industry due to their similar physicochemical properties. While open-metal sites (OMSs) in metal-organic frameworks (MOFs) are known to possess high affinity toward C\textsubscript{2}H\textsubscript{2}, its selective adsorption performance regulated by the electronic state of the same OMSs remains unexplored. Here, we report a metal electronic-state manipulation approach to construct a pair of isostructural Fe-MOFs, namely LiFM-26(Fe\textsubscript{II}/Fe\textsubscript{III}) and LiFM-27(Fe\textsubscript{III}) with different Fe\textsubscript{II} or Fe\textsubscript{III} oxidation states on the Fe centers, which display mixed-valent Fe\textsubscript{II}/Fe\textsubscript{III} centers in the former and sole Fe\textsubscript{III} centers in the latter. Remarkably, LiFM-26(Fe\textsubscript{II}/Fe\textsubscript{III}) shows significantly enhanced C\textsubscript{2}H\textsubscript{2} uptake capacity than LiFM-27(Fe\textsubscript{III}), attested by adsorption isotherms and IAST calculations, as well as simulated and experimental breakthrough experiments. Furthermore, in situ infrared (IR) and molecular calculations unveil that the presence of Fe\textsubscript{II} in LiFM-26(Fe\textsubscript{II}/Fe\textsubscript{III}) results in stronger Fe\textsubscript{II}–C\textsubscript{2}H\textsubscript{2} interactions than Fe\textsubscript{III}–C\textsubscript{2}H\textsubscript{2}, which plays a key role in the C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2} separation.

INTRODUCTION
Industrial chemical separations account for 10%–15% of the global energy consumption, which corresponds to half of the United States’s industrial energy use. Among them, acetylene (C\textsubscript{2}H\textsubscript{2}) purification represents an energy- and cost-intensive process. As one of the most widely used feedstocks in the petroleum industry, C\textsubscript{2}H\textsubscript{2} is mainly produced by the combustion of methane or thermal cracking of petroleum, with CO\textsubscript{2} as the major byproduct. Therefore, separating CO\textsubscript{2} from C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2} gas mixture is of great importance. Presently, the industrial separation of CO\textsubscript{2} from C\textsubscript{2}H\textsubscript{2} is usually implemented through solvent extraction and cryogenic distillation, leading to intensive costs and energy penalties due to their similar physicochemical properties (molecular sizes and shapes: 3.32 x 3.34 x 5.70 Å\textsuperscript{3} for C\textsubscript{2}H\textsubscript{2}, 3.18 x 3.33 x 5.36 Å\textsuperscript{3} for CO\textsubscript{2}; boiling points: 189.3 and 194.7 K for C\textsubscript{2}H\textsubscript{2} and CO\textsubscript{2}, respectively). As a result, adsorptive separation based on porous solid materials has drawn much attention owing to the advantage of dramatically reducing the energy and cost consumption. 5–10

Owing to their structural diversity, designable pore size, high pore volume, and tunable functionalities, metal-organic frameworks (MOFs) have shown great

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potentials in gas adsorption and separation involving C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8}, N\textsubscript{2}/O\textsubscript{2}, CO/H\textsubscript{2}, and CO/N\textsubscript{2}.\textsuperscript{8–15} However, it is still challenging to rationally design MOFs for C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2} separation due to their similar dynamic sizes and volatility. Tremendous efforts have been devoted to developing highly effective MOF adsorbents, suggesting that the introduction of open-metal sites (OMSs) into suitable pore space is most likely to be competent for this task.\textsuperscript{16–24} The suitable pore space (appropriate pore size, high pore volume, and polar pore surface) can render the framework with a high C\textsubscript{2}H\textsubscript{2} adsorption working capacity and facilitates adsorption dynamics.\textsuperscript{25–30} In addition, the OMSs with exposed partial positive charges not only behave as Lewis-acid-accepting electrons from the electron lone pair orbital of C\textsubscript{2}H\textsubscript{2} but also function as a p-bond back donor providing electrons to C\textsubscript{2}H\textsubscript{2} (delocalizing d electrons to the antibonding \textpi* orbitals of C\textsubscript{2}H\textsubscript{2}), thus resulting in preferential adsorption toward C\textsubscript{2}H\textsubscript{2} over CO\textsubscript{2}.\textsuperscript{26,31–33} However, it is extremely difficult to combine exposed positive charges and strong p-bond back donors into a single material. Actually, most MOFs with OMSs present weak p-bond back donation due to their electron-poor metal centers, and only a few MOFs featuring exposed electron-rich metal centers are found to be suitable for p-bond back donation.\textsuperscript{32,34–36}

In order to functionalize MOFs with electron-rich OMSs for highly selective C\textsubscript{2}H\textsubscript{2} adsorption, it is anticipated that the manipulation of the mixed-valent electronic states of exposed metal centers in a suitable MOF pore space is an effective yet challenging strategy. The introduction of an appropriate low-valent metal center can impart enhanced p\-back donation, thereby facilitating the preferential C\textsubscript{2}H\textsubscript{2} adsorption over CO\textsubscript{2}, while the presence of a high-valent metal center can allow for facile desorption of CO\textsubscript{2} due to the moderate metal-adsorbate interactions. Herein, we report a pair of isostructural Fe-MOFs, namely LIFM-26(Fe\textsuperscript{II}/Fe\textsuperscript{III})\textsuperscript{37} and LIFM-27(Fe\textsuperscript{III}) (LIFM stands for Lehn Institute of Functional Materials) that possess pore spaces constructed from the same perchlorinated ligand (2,3,5,6-tetrachloride terephthalic acid [TCDC]) (Scheme S1) and oxidation-state variant Fe\textsuperscript{II}/Fe\textsuperscript{III} centers (Scheme 1). Both structures feature coordinately unsaturated Fe centers, in which the ratios of Fe\textsuperscript{II} and Fe\textsuperscript{III} can be purposely tuned through an in situ redox process (Scheme 1), endowing the isostructural Fe-MOFs with distinct C\textsubscript{2}H\textsubscript{2} selective adsorption performance. It is worth noting that LIFM-26(Fe\textsuperscript{II}/Fe\textsuperscript{III}) and LIFM-27(Fe\textsuperscript{III}) are interconvertible as the isostructures of (Fe\textsuperscript{II}/Fe\textsuperscript{III})\textsubscript{3}O(TFBDC)\textsubscript{3} (TFBDC = 2,3,5,6-tetrafluorobenzene-1,4-dicarboxylate),\textsuperscript{38} providing ideal examples for studying the inherent relationship between the metal electronic-state and adsorption performance. Compared with LIFM-27(Fe\textsuperscript{III}), the increased electron density in LIFM-26(Fe\textsuperscript{II}/Fe\textsuperscript{III}) affords much higher C\textsubscript{2}H\textsubscript{2} uptake capacity and superior C\textsubscript{2}H\textsubscript{2} selectivity over CO\textsubscript{2} in the low-pressure region, due to the stronger Fe\textsuperscript{II}-adsorbate interactions than Fe\textsuperscript{III}-C\textsubscript{2}H\textsubscript{2}, which illustrates that manipulation of the electronic-state of OMSs can lead to enhanced preferential C\textsubscript{2}H\textsubscript{2} adsorption.

![Scheme 1. Schematic synthetic route of Fe-MOF isostructures with different ratios of Fe\textsuperscript{II} and Fe\textsuperscript{III} centers through a metal electronic-state manipulation strategy](image-url)
Moreover, the combined studies of ideal adsorbed solution theory (IAST) calculations, simulated/experimental dynamic breakthrough experiments, molecular simulations, and in situ infrared (IR) analysis well confirm that the exposed Fe[II] center with a strong π back-donation character plays a crucial role in the enhanced C_2H_2/CO_2 separation.

RESULTS AND DISCUSSION

Synthesis and structure determination
LIFM-26(Fe[II]/Fe[III]) was synthesized according to our previously reported method with a slight modification. The slow diffusion of triethylamine vapor into a mixture of N,N′-dimethylformamide (DMF) and water dissolving TCDC ligand and FeCl_2 for 3 days afforded LIFM-26(Fe[II]/Fe[III]) crystals, during which Fe[II] was partially oxidized into Fe[III]. In comparison, LIFM-27(Fe[III]) was obtained by extending the vapor diffusion time to 1 month, during which Fe[II] was completely oxidized into Fe[III] (Scheme 1). Notably, LIFM-27(Fe[III]) can be transformed back to LIFM-26(Fe[II]/Fe[III]) via soaking the samples in ethanol solution for 3 days at 75°C (denoted as LIFM-27(Fe[III])-EtOH; Figure S10), showing solvent-dependent redox property. Single-crystal X-ray diffraction (SCXRD) analyses reveal that LIFM-26(Fe[II]/Fe[III]) and LIFM-27(Fe[III]) crystallize in the P-3 and P21/n space groups, respectively (Table S1). Both of them possess the same acs net topology as (Fe[II]/Fe[III])_3O(TFBDC)_3, which is constructed from perfluorinated ligand TFBDC and FeCl_2 (Figure 1).

In order to probe the oxidation and spin states of Fe centers, ^{57}Fe Mössbauer spectroscopic experiments were carried out for LIFM-26(Fe[II]/Fe[III]), LIFM-27(Fe[III]), and LIFM-27(Fe[III])-EtOH (Figures 2 and S3–S5; Table S2). The spectra of LIFM-26(Fe[II]/Fe[III]) can be fitted by one type of doublet and one type of singlet, revealing two kinds of Fe species with adsorption area ratios of 47.65% and 52.35%, corresponding to the amounts of Fe[II] and Fe[III] centers (0.9:1.0) (Figure 2A, D1 line). For comparison, only one type of fitting doublet in LIFM-27(Fe[III]) was observed, confirming the existence of sole Fe[III] species (Figure 2B). LIFM-27(Fe[III])-EtOH also shows two kinds of Fe species similar to LIFM-26(Fe[II]/Fe[III]) yet with different adsorption area ratios, implying a variation of Fe[II] and Fe[III] species (Fe[II]:Fe[III] = 0.5:1.0; Figure S5). As shown in Figure 2A, the D2 line can readily be assigned to high-spin Fe[III] species in LIFM-26(Fe[II]/Fe[III]) with isomer shift δ = 0.78 mm/s, while the D3 line can be assigned to medium-spin Fe[II] species with isomer shift δ = 0.31 mm/s and quadrupole splitting value

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DEQ = 0.56 mm/s, suggesting the existence of a strong π back donation in LIFM-26(Fe[II]/Fe[III]). For LIFM-27(Fe[III]), the Mössbauer spectra reveal only one type of high-spin Fe[III] species with isomer shift δ = 0.44 mm/s.

Purity and porosity
Powder X-ray diffraction (PXRD) patterns were conducted to confirm the phase purity of the as-synthesized samples (Figures S8, S9, and S11), and the scanning electron microscope (SEM) images unveil similar crystal morphology (Figure S7). Thermal gravimetric analyses (TGAs) indicate comparable thermal stability of two isostructural MOFs up to 250°C (Figure S6). In contrast to (Fe[II]/Fe[III])₃O(TFBDC)₃ (Figure S11), both LIFM-26(Fe[II]/Fe[III]) and LIFM-27(Fe[III]) retain good crystallinity after activation under high vacuum, indicative of their good framework robustness (Figures S8 and S9). N₂ sorption isotherms at 77 K were collected to evaluate the permanent porosity of all three samples. As shown in Figure 3A, LIFM-26(Fe[II]/Fe[III]) (356 cm³ g⁻¹) and LIFM-27(Fe[III]) (310 cm³ g⁻¹) show much higher N₂ uptakes than (Fe[II]/Fe[III])₃O(TFBDC)₃ (17 cm³ g⁻¹) due to loss of its crystallinity after activation (Figure S11). Both LIFM-26(Fe[II]/Fe[III]) and LIFM-27(Fe[III]) show typical type I adsorption isotherms with the Brunauer-Emmett-Teller (BET) surface areas of 1,403 and 1,174 m² g⁻¹, respectively, and the total pore volumes are 0.55 and 0.48 cm³ g⁻¹, respectively (Figures S12–S14; Table S3). The pore sizes of
LIFM-26(Fe[II]/Fe[III]) are calculated to be 6.8, 8.0, and 10.1 Å by density functional theory (DFT) analysis, while those of LIFM-27(Fe[III]) are 6.8 and 8.0 Å (Figure S15), matching well with the corresponding structural analyses. Additionally, we also evaluated the porosity of LIFM-27(Fe[III])-EtOH, which exhibits the BET surface area and pore volumes of 1,330 m² g⁻¹ and 0.53 cm³ g⁻¹, falling between those of LIFM-26(Fe[II]/Fe[III]) and LIFM-27(Fe[III]) (Figure S16; Table S4).

**Adsorption studies**

The suitable pore structures of two isostructural Fe-MOFs as described above, including appropriate pore size and high pore volume as well as polar pore surface, are anticipated to facilitate C₂H₂ adsorption. To examine the effectiveness of the variant electronic state of OMSs on the adsorption performance, we selected C₂H₂ as a model gas molecule for evaluation. The C₂H₂ adsorption isotherms of both MOFs were measured at 273, 285, and 298 K, respectively (Figures 3B, 3C, S17, S19–S21, and S23–S24). Evidently, LIFM-26(Fe[II]/Fe[III]) showed much higher C₂H₂ uptake capacity (181 and 131 cm³ g⁻¹ at 273 and 298 K, 1 bar, respectively) than LIFM-27(Fe[III]) (128 and 97 cm³ g⁻¹ at 273 and 298 K, 1 bar, respectively), suggesting that Fe[II] center with higher electron density for stronger π back donation in LIFM-26(Fe[II]/Fe[III]) can effectively improve its adsorption behavior. Specifically, LIFM-26(Fe[II]/Fe[III]) (17.0 cm³ g⁻¹) can take up more than four times of C₂H₂ than LIFM-27(Fe[III]) (4.2 cm³ g⁻¹) at low pressure (3.4 mbar) (Figure 3D). Moreover, the C₂H₂ uptake capacity of LIFM-26(Fe[II]/Fe[III]) is much higher than that of (Fe[II]/Fe[III]₃(TFBDC)₃ (Figures 3B and S25), and is also higher than many other known MOFs like Zn-MOF-74 (122 cm³ g⁻¹), UTSA-74a (104 cm³ g⁻¹), UTSA-74b (122 cm³ g⁻¹), and PCP-33 (122 cm³ g⁻¹), but is lower than some MOFs like FJI-H8-R series (174–229 cm³ g⁻¹), MIL-160 (191 cm³ g⁻¹), SIFSIX-Cu-TPA (185 cm³ g⁻¹), and FJU-90a (180 cm³ g⁻¹) (Table S5). To further confirm the effect of low-valent Fe[II] center, the C₂H₂ adsorption of LIFM-27(Fe[II]/Fe[III])-EtOH, in which the amount of Fe[II] center is less than the prototypical LIFM-26(Fe[II]/Fe[III]), was measured at 298 K. As expected, the C₂H₂ uptake by LIFM-27(Fe[II]/Fe[III])-EtOH was lower than LIFM-26(Fe[II]/Fe[III]) but higher than LIFM-27(Fe[III]) (Figures S30–S32). Additionally, the CO₂ adsorption isotherms were performed on both Fe-MOFs. LIFM-26(Fe[II]/Fe[III]) can take up 80 cm³ g⁻¹ CO₂ at 298 K and 1 bar, while the uptake capacity of LIFM-27(Fe[III]) is 51 cm³ g⁻¹ under the same condition (Figures 3B, 3C, S18, and S22).
results indicate that the gas adsorption performance of the two isostructural Fe-MOFs can be finely tuned by regulating the electron state of OMSs. Furthermore, the continuous C$_2$H$_2$ and CO$_2$ adsorption isotherms on both Fe-MOFs were carefully performed, verifying their excellent reusability (Figures 3E, 3F, and S26–S29).

The isosteric heat ($Q_{st}$) of C$_2$H$_2$ and CO$_2$ on both MOFs were calculated using the Clausius-Clapeyron equation based on their adsorption isotherms at three different temperatures (Figures S17, S18, S21, S22, and S33–S36). For C$_2$H$_2$, LIFM-26(Fe$^{II}$/Fe$^{III}$) displays higher isosteric heat (53.8 kJ mol$^{-1}$) than LIFM-27(Fe$^{III}$) (44.6 kJ mol$^{-1}$) at near-zero coverage corresponding to the interactions between gas and Fe center, which further confirms the electronic effect of the open Fe$^{II}$ centers (Figures S37 and S38). Afterward, the subsequent gradual decrease in isosteric heat for C$_2$H$_2$ on both MOFs along with increased C$_2$H$_2$ loading amount indicate the adsorption saturation of Fe centers. Notably, the moderate $Q_{st}$ value of C$_2$H$_2$ in LIFM-26(Fe$^{II}$/Fe$^{III}$) is lower than some other reported MOFs with OMSs, such as ATC-Cu (79.1 kJ mol$^{-1}$),$^{16}$ Cu@ UiO-66(COOH)$_2$ (74.5 kJ mol$^{-1}$),$^{43}$ ZJU-74a (65.0 kJ mol$^{-1}$),$^{44}$ and NKMOF-1-Ni (60.3 kJ mol$^{-1}$),$^{45}$ implying the sufficient adsorption reversibility of the adsorbent owing to the presence of Fe$^{III}$ center. For CO$_2$, both MOFs present comparable isosteric heats, giving values of 37.8 (LIFM-26(Fe$^{II}$/Fe$^{III}$)) and 35.8 kJ mol$^{-1}$ (LIFM-27(Fe$^{III}$)) at near-zero coverage (Figures S37 and S38). The higher $Q_{st}$ value of C$_2$H$_2$ than CO$_2$ suggests a promising potential of C$_2$H$_2$ purification from C$_2$H$_2$/CO$_2$ gas mixture.
Adsorption mechanism

To probe the binding interaction of C$_2$H$_2$ with the frameworks, in situ IR spectroscopy measurements were performed. The samples of LIFM-26(Fe[II]/Fe[III]) and LIFM-27(Fe[III]) were first heated under vacuum to remove trapped solvents and then cooled to room temperature to collect IR spectra of activated samples, as presented in Figure 4A. The spectra of two samples are dominated by the vibrational bands associated with the organic linker (Figure S44), which exhibit general similarities. A noticeable difference is that the LIFM-27(Fe[III]) sample shows extra two bands at ~3,634 and 820 cm$^{-1}$, which are absent in LIFM-26(Fe[II]/Fe[III]). Based on the well-established studies on Fe-based MOFs containing a hydroxyl group, these two bands are attributed to the stretching and deformation modes of OH$^-$, which terminates one Fe[III] of the trimeric Fe[III]$_3$O cluster for charge balance. In the neutrally charged (Fe[II]/Fe[III])$_3$O cluster of the LIFM-26(Fe[II]/Fe[III]) sample, no extra OH$^-$ is needed. In addition, careful examination of spectra at 1,600–1,500 cm$^{-1}$ reveals that carboxylate asymmetric stretching band $v$$_{as}$(COO) in LIFM-26(Fe[II]/Fe[III]) occurs at a higher frequency (1,590 cm$^{-1}$) than that in the LIFM-27(Fe[III]) sample, leading to a larger separation $\Delta v$ between $v$$_{as}$(COO) and $v$$_d$(COO). This is as expected since the inequivalence of the two C–O bonds connected with Fe[II] and Fe[III], respectively, would further split $\Delta v$. Gas adsorption measurement was then conducted on these activated samples by loading C$_2$H$_2$ at ~1 bar for ~10 min to ensure adsorption saturation, which was followed by subsequent desorption via pumping the samples under vacuum. The adsorbed C$_2$H$_2$ is clearly observed in different IR spectra (Figure 4B), which demonstrate the characteristic stretching band $v$$_{as}$(C$_2$H$_2$) of adsorbed C$_2$H$_2$ at 3,400–3,200 cm$^{-1}$. A marked difference is noted for both the position and shape of the $v$$_{as}$(C$_2$H$_2$) band between in LIFM-26(Fe[II]/Fe[III]) and LIFM-27(Fe[III]). LIFM-27(Fe[III]) displays only a single band located at 3,237 cm$^{-1}$, which corresponds to C$_2$H$_2$ adsorbed at the primary exposed Fe[III] sites, as identified by molecular simulations (Figures 5B and S46; vide infra). In comparison, LIFM-26(Fe[II]/Fe[III]) shows two distinct bands appearing at higher frequencies of 3,374 and 3,286 cm$^{-1}$, pointing to two types of C$_2$H$_2$. 

![Figure 4](https://via.placeholder.com/150)
adsorbed on Fe[II] and Fe[III] sites, respectively. It is noteworthy that the 3,374 cm\(^{-1}\) band undergoes an upward shift (blue shift) with respect to the value of the gas phase C\(_2\)H\(_2\) (3,287 cm\(^{-1}\)).\(^{51}\) Such a shift to the higher wavenumber strongly suggests that \(\pi\)-back donation occurs between Fe[II] cations and C\(_2\)H\(_2\) in LIFM-26(Fe[II]/Fe[III]),\(^{52}\) which weakens the C–C bond but stiffens the C–H bond,\(^{53}\) thus resulting in a raise of C–H stretching frequency. The broadening and asymmetric line shape of the \(v_{as}(C_2H_2)\) bands in LIFM-26(Fe[II]/Fe[III]) indicate vibrational dynamic coupling between adsorbed C\(_2\)H\(_2\) molecules, which could account for the occurrence of the Fe[III]-bound C\(_2\)H\(_2\) band at a higher frequency of 3,286 cm\(^{-1}\) in LIFM-26(Fe[II]/Fe[III]) compared with that in LIFM-27(Fe[III]) (3,237 cm\(^{-1}\)).\(^{54}\)

To get further insight into the adsorption mechanism with regard to the mixed-valent Fe[II]/Fe[III] centers, we implemented molecular simulations. For LIFM-26(Fe[II]/Fe[III]), C\(_2\)H\(_2\) is mainly located in the channel surrounded by one open Fe[II] center and two chlorine atoms, in which the strong Fe\(\cdots\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·
of the increased electron density at the Fe[II] center. Subsequently, the C$_2$H$_2$/CO$_2$ selectivity for both MOFs gradually decreases as a function of the increased pressure due to the adsorption saturation of the Fe centers. The final C$_2$H$_2$/CO$_2$ selectivities for LIFM-26(Fe[II]/Fe[III]) and LIFM-27(Fe[III]) are 4.8 and 5.5 at 298 K and 1 bar, respectively, which are comparable with many reported MOFs, such as SIFSIX-Cu-TPA (5.3),$^{41}$ SNNU-45 (4.5),$^{56}$ TIFSIX-2-Cu-i (6.5),$^{28}$ FJU-90 (4.3),$^{42}$ UTSA-222 (4.0),$^{57}$ JNU-1 (3.6),$^{18}$ and Zn-MOF-74 (2.8).$^{31}$ Additionally, the C$_2$H$_2$ uptake capacity was calculated based on the IAST method. Compared with LIFM-27(Fe[III]) (4.7 cm$^3$ g$^{-1}$ at 0.01 bar), LIFM-26(Fe[II]/Fe[III]) exhibits enhanced C$_2$H$_2$-capture performance, especially at low pressure (20.4 cm$^3$ g$^{-1}$ at 0.01 bar) (Figure 6B). More importantly, the C$_2$H$_2$ uptake capacity for both MOFs is remarkably higher than their CO$_2$ adsorption, implying potential C$_2$H$_2$-separation ability from C$_2$H$_2$/CO$_2$ mixture (Figure 6B).

Prompted by the outstanding C$_2$H$_2$ uptake capacity and C$_2$H$_2$/CO$_2$ adsorption selectivity, the simulated transient breakthrough experiments were carried out...
according to the documented methodology. For both LiFM-26(Fe[II]/Fe[III]) and LiFM-27(Fe[III]), CO₂ elutes first, and then C₂H₂ breaks through after some time, demonstrating the adequate capacity for the demanding C₂H₂/CO₂ separation (Figures S52 and S53). The C₂H₂ capture productivity calculated on the basis of the simulated breakthrough curves gives rise to the values of 88.9 (LiFM-26(Fe[II]/Fe[III])) and 76.6 (LiFM-27(Fe[III])) cm³ g⁻¹, unveiling the better C₂H₂/CO₂-separation performance of LiFM-26(Fe[II]/Fe[III]). It is noticeable that the C₂H₂ productivity for LiFM-26(Fe[III]/Fe[III]) is slightly lower than FJU-90 (114.2 cm³ g⁻¹) yet higher than other reported MOFs including FJU-22a (83.1 cm³ g⁻¹), ZUL-60a (80.6 cm³ g⁻¹), UTSA-74a (79.7 cm³ g⁻¹), Zn-MOF-74 (76.6 cm³ g⁻¹), and PCP-33 (75.7 cm³ g⁻¹).

To further assess the practical C₂H₂/CO₂-separation performance by both LiFM-26(Fe[II]/Fe[III]) and LiFM-27(Fe[III]), dynamic fixed-bed breakthrough experiments were conducted through a stainless-steel column under ambient condition, in which the equimolar C₂H₂/CO₂ mixture flowed over the packed column with a flow rate of 1.0 mL min⁻¹. As depicted in Figure 6C, both Fe-MOFs present excellent C₂H₂-separation performance from C₂H₂/CO₂ mixture. For LiFM-26(Fe[II]/Fe[III]), CO₂ undoubtedly elutes first and then quickly reaches a pure grade without detectable C₂H₂, while C₂H₂ remains in the packed column for a remarkable time until it is saturated in LiFM-26(Fe[II]/Fe[III]). As expected, LiFM-27(Fe[III]) exhibits similar C₂H₂/CO₂ dynamic breakthrough behavior but with a shorter C₂H₂ breakthrough time. Based on the experimental breakthrough curves, LiFM-26(Fe[II]/Fe[III]) and LiFM-27(Fe[III]) present comparable C₂H₂/CO₂ selectivity with values of 1.6 and 1.7, respectively. The calculated C₂H₂-capture productivity for LiFM-26(Fe[II]/Fe[III]) is estimated to be 60.0 cm³ g⁻¹, whereas the value for LiFM-27(Fe[III]) is 53.7 cm³ g⁻¹. In principle, ideal adsorbents should present good recyclability in practical industrial applications. Therefore, the continuous dynamic breakthrough experiments were performed under the above conditions. The results indicate that both Fe-MOFs maintain almost the same retaining time and capture productivity in three continuous C₂H₂/CO₂ dynamic breakthrough experiments (Figures 6D, S50, and S51), demonstrating their good reusability. The PXRD patterns after the repetitive experiments also confirm the crystallinity is retained well (Figures S54 and S55). Taken together, these results clearly demonstrate that the Fe-MOFs have successfully achieved a combination of high C₂H₂ uptake capacity, moderate-high C₂H₂/CO₂ selectivity, and sufficient reversibility by rationally regulating the electronic state of the open-metal centers.

In summary, a metal electronic-state manipulation strategy has been successfully applied to constructing a pair of microporous isostructural Fe-MOFs featuring open Fe centers with different electron densities for efficient C₂H₂/CO₂ separation. Notably, the isostructural LiFM-26(Fe[II]/Fe[III]) and LiFM-27(Fe[III]) can be interconverted, and the electronic state of Fe centers can be finely tuned by simply changing the oxidation conditions depending on the solvents and reaction time, thus facilitating understanding of the inherent relationship between the metal electronic state and C₂H₂ selective adsorption. Compared with LiFM-27(Fe[III]), LiFM-26(Fe[II]/Fe[III]) presents remarkably higher C₂H₂ uptake capacity while retaining moderate-high C₂H₂/CO₂ selectivity, which is well supported by the simulated and experimental dynamic breakthrough experiments. In situ IR and molecular calculations manifest that LiFM-26(Fe[II]/Fe[III]) exhibits enhanced binding affinity toward C₂H₂ than LiFM-27(Fe[III]) due to the increased electron density at the metal site, resulting in a stronger π back donation. Significantly, this work provides an effective guideline to realize the challenging C₂H₂/CO₂ separation by rationally manipulating the electronic state of OMSs in MOF pore spaces.
MATERIALS AND METHODS
See the supplemental experimental procedures for full details of synthesis, characterization, modeling and analysis, and adsorption and breakthrough measurements.

EXPERIMENTAL PROCEDURES

Resource availability
Lead contact
Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Cheng-Yong Su (casscy@mail.sysu.edu.cn), and Shengqian Ma (shengqian.ma@unt.edu).

Materials availability
All materials generated in this study are available from the lead contact without restriction.

Data and code availability
The X-ray crystallographic coordinates for LIFM-27(Fe[III]) have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under CCDC: 2114493. These data can be obtained free of charge from the CCDC via http://www.ccdc.cam.ac.uk/data_request/cif. All other data are available from the lead contact upon request.

SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.xcrp.2022.100977.

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AUTHOR CONTRIBUTIONS

DECLARATION OF INTERESTS
The authors declare no competing interests.

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