Chemistry A European Journal



European Chemical Societies Publishing

Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Eur. J. 10.1002/chem.202101053

Link to VoR: https://doi.org/10.1002/chem.202101053



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Optimizing Fe-based Metal-Organic Frameworks through Ligand Conformation Regulation for Efficient Dye Adsorption and C₂H₂/CO₂ Separation

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Abstract: Regulating the structure of metal-organic frameworks (MOFs) by adjusting the ligands reasonably is expected to enhance the interaction of MOFs on special molecules/ions, which has significant application value for the selective adsorption of guest molecules. In this work, two tricarboxylic ligands H₃L-Cl and H₃L-NH₂ were designed and synthesized based on the ligand H₃TTCA by replacing part of the benzene rings with C=C bonds and modifying the chlorine and amino groups on the 4-position of the benzene ring. Two 3D Fe-MOFs (UPC-60-Cl and UPC-60-NH₂) with the novel topology types were constructed. As the C=C bonds of the ligands have flexible torsion angles, UPC-60-CI features three types of irregular 2D channels, while UPC-60-NH₂ has a cage with two types of windows on the surface. The synergistic effect of unique channels and modification of functional groups endows UPC-60-CI and UPC-60-NH2 with high adsorption capacity for organic dyes. UPC-60-CI shows high adsorption capacity for CV (147.2 mg g⁻¹), RHB (100.3 mg g⁻¹), and MO (220.9 mg g⁻¹), while UPC-60-NH₂ exhibits selective adsorption of MO (158.7 mg g⁻¹). Meanwhile, based on the diverse pore structure and modification of active sites, UPC-60-CI and UPC-60-NH₂ show the selective separation of equimolar C_2H_2/CO_2 . Therefore, reasonable regulation of organic ligands plays a significant role in guiding the structure diversification and performance improvement of MOFs.

Introduction

As a new porous material in the recent two decades, metalorganic frameworks (MOFs) have a wide range of potential applications in many fields (such as gas adsorption/separation, catalysis, and fluorescence recognition) due to their various structures and high specific surface area.[1-8] Compared with traditional porous materials, one of the most attractive features of MOFs is the tunability of their structure and pore environment. For the specific molecules/ions like organic dyes and gases, the structure and channel of MOFs can be precisely regulated by controlling the shape and length of organic ligands to achieve the selective adsorption of molecules with different sizes.^[9-14] In addition, by modifying flexible functional groups or introducing groups with steric hindrance effects in specific positions of rigid ligands, various conformations are expected to form during the self-assembly process, which provides opportunities for obtaining MOFs with novel structures.^[15-18] In our previous work, by modifying tetracarboxylic ligand H₄DCBA with -CH₃/-CF₃ groups, the torsion angle of the central benzene ring in the ligand was changed, and then the topologies of UPC-48-50 were successfully adjusted to optimize the separation of specific molecules/ions.^[19]



Figure 1. (a) The ligands H_3L -Cl and H_3L -NH₂ which synthesized by modification of H_3TTCA with C=C bond, -Cl and -NH₂ group. (b-e) Conformations of the ligands in MOFs. (Blue plane: the relative plane of the central phenyl rings. The atom C, O, N, and Cl are represented by gray, red, blue, and green, respectively.)

Moreover, the pore environment can be optimized through functional modification of metal nodes or organic ligands, thereby enhancing the host-guest interaction and achieving the separation of different molecules/ions with specific chemical properties.^[20-25] The modification of clusters or ligands has great potential in removing pollutants such as dyes in wastewater. The amount of textile dyes discharged globally each year far exceeds the natural purification capacity, so there is an urgent to develop

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Figure 2. (a) The structure and simplified form of SBU and ligands. (b,c) The structure of UPC-60-CI (b) and the three kinds of channels (c). (d,e) The structure of UPC-60-NH₂ (d) and the cage (e) which formed by 12 SBUs and 12 ligands. (H atoms are omitted for clarity.)

effective organic dye adsorbents.^[26-28] In addition to the higher specific surface area and porosity, the active sites such as -NH2 and -SH in the channel of MOFs also increase the interaction (such as hydrogen bonding interaction, π - π interaction, etc.) between the framework and the dye molecule.^[29-32] With the discovery of a series of water-stable MOFs, they are gradually used to remove toxic organic dyes in water.^[33-35] At the same time, the optimized pore environment is also of great application value to the separation and purification of light hydrocarbon gas in the petrochemical industry.^[36,37] For instance, C₂H₂ produced from hydrocarbon pyrolysis is usually mixed with impurity gases such as CO₂, but their similar physical properties make it difficult to separate by conventional separation techniques (such as cryogenic distillation, liquid adsorption, etc.) with large energy consumption and low efficiency. MOFs are used as adsorbents gas separation represents an energy-efficient and for environmentally friendly separation technology due to their tunable pore apertures to enforce functionalized pore environments to selectively accommodate specific gas molecules.[38-40]

Herein, based on rigid tricarboxylic ligand H₃TTCA ([1,1':3',1"terphenyl]-4,4",5'-tricarboxylic acid), we increased the flexibility of the ligand by replacing part of the benzene rings with C=C bonds, thus presenting multiple conformations for the ligand and increasing the structural diversity of MOFs (Figure 1). Moreover, the ligands were modified with -Cl and -NH₂ to increase their functionality. Finally, two tricarboxylic ligands H₃L-Cl (4-chlorine-3,5-bis(2-carboxyethenyl)benzoic acid) and H₃L-NH₂ (4-amino-3,5-bis(2-carboxyethenyl)benzoic acid) were successfully designed and synthesized, and two 3D Fe-MOFs (UPC-60-CI and successfully **UPC-60-NH**₂) were constructed through solvothermal reaction. Diverse channels and functionalized active sites make UPC-60-CI and UPC-60-NH2 show high adsorption capacity for dyes and good selectivity for C₂H₂/CO₂.

Results and Discussion

Crystal structures of UPC-60-CI and UPC-60-NH₂

Single crystal X-ray diffraction (SCXRD) revealed that UPC-60-CI crystallizes in the tetragonal space group P4₃2₁2. Each Fe³⁺ is connected to a μ_3 -O atom, a water molecule, and four O atoms from different L-Cl³⁻ ligands. Three Fe³⁺ are connected through µ₃-O atom and coordinate with six different ligands to form a classic [Fe₃O(COO)₆(H₂O)₃] cluster. The asymmetric unit of UPC-60-CI contains one and a half crystallographically independent Fe(III) atoms, a deprotonated L-Cl³⁻ ligand, a half $\mu_3\text{-}O$ atom, and one and a half H₂O molecules. Compared with UPC-200(Fe)-H-H₂O constructed by the rigid ligand H_3TTCA and $[Fe_3O(COO)_6(H_2O)_3]$ cluster,^[41] the C=C bonds of UPC-60-CI are distorted by 10.513° and 35.573° during the self-assembly process, resulting in the change of crystal structure (Figure 2b). From the a,b-axis, there are three types of irregular channels in UPC-60-CI, the apertures of large (A), middle (B), and small (C) channels are 7 x 7 Å², 4.5 \times 8 Å², and 4 \times 4.5 Å², respectively, and the -Cl group is modified in the channel A and B (Figure 2c). From a topological point of view, the SBUs and ligands are simplified to 6-connected nodes and 3-connected nodes, respectively. The topological analysis shows that the structure of UPC-60-CI can be simplified to a novel 2-nodal (3,6-c)-connected topology with the point symbol of {6¹¹·8⁴}{6³}₂ (Figure S3d). Using the SQUEEZE program in the PLATON software, the solvent availability of UPC-60-CI is calculated to be 60.70% (3696.5 Å of 6091.8 Å unit cell volume), and the density is 0.8994 g cm⁻³.

 $\mbox{UPC-60-NH}_2$ crystallizes in the cubic space group Im-3. The asymmetric unit of $\mbox{UPC-60-NH}_2$ contains one and a half crystallographically independent Fe(III) atoms, a deprotonated L-

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NH₂³⁻ ligand, a half µ₃-O atom, and one and a half H₂O molecules. Fe³⁺ is connected with H₃L-NH₂ ligand to form the same [Fe₃O(COO)₆(H₂O)₃] cluster as UPC-60-CI. During the crystal formation process, H₃L-NH₂ has two different conformations with two torsion angles of 14.700° and 28.515° for the C=C bond, respectively, and finally a 3D framework is obtained (Figure 2d). It is worth noting that the framework of UPC-60-NH2 encloses a cage composed of 12 SBUs and 12 ligands with a volume of 18 Å³ (Figure 2e). Interestingly, there are two types of windows on the surface of the cage, and the sizes of windows are 2.6×7.0 Å² and 6.0 × 6.0 Å², respectively. The former is modified with -NH₂ which points to the inside of the window. The topological analysis shows that the structure of UPC-60-NH2 can be simplified to a novel 3-nodal (3,3,6-c)-connected topology with the point symbol of {4·6²}₂{4²·6⁷·8⁶} (Figure S3f). Using the SQUEEZE program in the PLATON software, the solvent availability of UPC-60-NH2 is calculated to be 61.20% (24915.1 Å of 40687.4 Å unit cell volume) and the density is 0.7719 g cm⁻³.



Figure 3. The N_2 adsorption diagram of UPC-60-Cl (a) and UPC-60-NH₂ (b) at 77 K (inside: aperture distribution).

Permanent porosity

Powder X-ray diffraction (PXRD) and thermogravimetric (TG) analysis confirmed the phase purity and thermal stability of **UPC-60-CI** and **UPC-60-NH**₂ (Figure S4,5). The multiple channels and cages in the frameworks prompted us to test the porosity of **UPC-60-CI** and **UPC-60-NH**₂. Figure 3 shows that **UPC-60-CI** and **UPC-60-NH**₂ exhibited type I N₂ adsorption isotherms, and their maximum adsorption capacities are 341.8 cm³ g⁻¹ and 405.3 cm³ g⁻¹, respectively. The Brunauer-Emmett-Teller (BET) and pore distribution are 1067.9 m² g⁻¹ and 5.8, 6.8, 11 Å for **UPC-60-CI**, and 1692.4 m² g⁻¹ and 8, 10 Å for **UPC-60-NH**₂, respectively.



Figure 4. (a) The maximum adsorption capacity of dye molecules by UPC-60-CI and UPC-60-NH₂. (b) The effect of time on the dye molecules adsorption by UPC-60-CI and UPC-60-NH₂.

Dye adsorption

In recent years, water-stable MOFs have been widely used to remove organic dyes from water based on their unique pore structure, electrostatic adsorption, hydrogen bonding interaction, etc.^[42-47] To explore the adsorption capacity of **UPC-60-CI** and **UPC-60-NH**₂ for different dyes, five organic dyes include Rhodamine B (RHB, 6.53 × 11.89 × 15.55 Å³), Crystal violet (CV, 4.77 × 12.43 × 13.09 Å³), Xylenol orange (XO, 8.86 × 10.02 × 14.17 Å³), Methyl orange (MO, 4.14 × 5.65 × 13.65 Å³), and Chrome Blue K (CBK, 4.48 × 8.60 × 14.82 Å³) is selected for adsorption tests. Among them, RHB and CV exhibit positive charges, XO exhibit neutral charges, MO, and CBK exhibit negative charges, respectively. The molecular structures of the five dyes are shown in Figure S8.

As shown in Figure 4a, due to the differences in channels and functional groups, UPC-60-CI and UPC-60-NH2 show specific dye adsorption effects. Among them, UPC-60-CI has an excellent adsorption effect on CV, RHB, and MO, with the maximum adsorption capacity reaching 147.2, 100.3, and 220.9 mg g⁻¹, respectively, which is comparable to the Fe@Cu-MOF-2COOH (MO: 225.1 mg g⁻¹)^[48] and higher than Cd-based MOF (MO: 166.7 mg g⁻¹)^[49], but lower than PCN-222 (MO: 589 mg g⁻¹)^[50]. This adsorption performance may be due to the multiple channel structures and environments having different adsorption effects on the dye molecules of different sizes. However, UPC-60-NH2 exhibits selective adsorption of MO with a maximum adsorption capacity of 158.7 mg g⁻¹, while other larger organic dyes have extremely low or no adsorption capacity, which may be attributed to the synergy of appropriate cage size, hydrogen bond interactions between -NH₂ and MO, and the π - π stacking

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Figure 5. (a) Single component C_2H_2 and CO_2 adsorption data at 298 K for UPC-60-CI; (b) Single component C_2H_2 and CO_2 adsorption data at 298 K for UPC-60-NH₂; (c,d) Breakthrough curves for C_2H_2/CO_2 (50:50) separations with UPC-60-CI (c) and UPC-60-NH₂ (d) at 1 atm and 298 K.

interaction. The high adsorption capacities are comparable to some reported MOFs (Table S4). In addition, the adsorption of **UPC-60-CI** and **UPC-60-NH**₂ on dyes can reach adsorption equilibrium quickly. After adding the sample, the characteristic peak of dye molecules decreased rapidly (Figure S7). Within 12 hours, the adsorption capacity of **UPC-60-CI** for CV, RHB, and MO reached 88.95%, 97.29%, and 99.93%, respectively, and the adsorption capacity of **UPC-60-NH**₂ for MO reached 99.02% (Figure 4b). The solution turns colorless, indicating that **UPC-60-CI** and **UPC-60-NH**₂ can quickly absorb organic dye molecules and reach saturation. PXRD analysis of **UPC-60-CI** and **UPC-60-NH**₂ samples after dye adsorption proved that the framework maintains high stability (Figure S9), which is expected to be further applied to the treatment of industrial dye wastewater.

Breakthrough experiments

Owing to the high porosity and tunable pore environment, **UPC-60-CI** and **UPC-60-NH**₂ demonstrated remarkable light hydrocarbons uptake (Figure S12). It is worth noting that there is a large difference in the adsorption capacity of C_2H_2 and CO_2 . As shown in Figure 5a,b, the maximum adsorption capacity of C_2H_2 and CO_2 are 100.3 and 51.6 cm³ g⁻¹ for **UPC-60-CI** and 116.4 and 60.0 cm³ g⁻¹ for **UPC-60-NH**₂ at 298 K and 1 bar, respectively. Therefore, we calculated the separation selectivity of **UPC-60-CI** and **UPC-60-NH**₂ for different component C_2H_2/CO_2 gases by using the Ideal Adsorption Solution Theory (IAST) method and calculated the isosteric heat of adsorption (Q_{st}) for different gases according to the Clausius-Clapeyron equation (Figure S13).

According to the calculation, UPC-60-CI and UPC-60-NH2 has excellent separation capacity, which better than PCN-207-FA (C₂H₂: 68.90 cm³ g⁻¹ and 32.47 kJ mol⁻¹)^[51], ZJNU-55a (C₂H₂: 56.3 cm³ g⁻¹ and 42.40 kJ mol⁻¹)^[52], and PCN-307 (CO₂: 73.3 cm³ g⁻¹ and 22.84 kJ mol⁻¹)^[53]. To further evaluate the practical C₂H₂/CO₂ separation performance of UPC-60-CI and UPC-60- NH_2 , we tested the breakthrough of equimolar C_2H_2/CO_2 gas mixtures upon UPC-60-CI and UPC-60-NH2 at 298 K and 1 bar. As shown in Figure 5c,d, C₂H₂/CO₂ is effectively separated through the fixed bed. CO₂ was first detected from the outlet gas with high purity, and no C₂H₂ was detected in this process. This adsorption property may be attributed to the different interaction forces of appropriate channel structure and environment on quest molecules. After 14 minutes, C2H2 reached saturation and breakthrough in the adsorbent, indicating that UPC-60-CI has good potential to separate C_2H_2/CO_2 in practical application. For **UPC-60-NH**₂, the effective separation time of C_2H_2/CO_2 is up to 20 min g⁻¹. The separation time of C_2H_2/CO_2 is comparable to some reported MOFs such as UTSA-300 (12.4 min g⁻¹)^[21] and UTSA-74 (27 min g^{-1)[54]} (Table S5). After four cycles of experiments, the UPC-60-CI and UPC-60-NH₂ still maintain excellent separation ability, which indicates that it has good cycling stability and is expected to be used in the actual industrial separation process.

Conclusion

In summary, two 3D Fe-based MOFs (UPC-60-CI and UPC-60-NH₂) with novel topology were synthesized based on two

tricarboxylic ligands H₃L-Cl and H₃L-NH₂ modified by C=C bond, -Cl, and -NH₂. The diversified structure and modification of functional groups enable **UPC-60-Cl** and **UPC-60-NH**₂ to show high adsorption capacity and adsorption rate for organic dyes. Meanwhile, the multiple channels and cages in the framework endow **UPC-60-Cl** and **UPC-60-NH**₂ with good separation ability for equimolar C₂H₂/CO₂ mixed gas. Through reasonable regulation of ligands with functional groups, the channels can be precisely regulated to achieve the adsorption and separation of specific guest molecules.

Experimental Section

Materials and measurement

All the chemical reagents were purchased from chemical vendors and were used without further purification. The crystal data of **UPC-60-CI** and **UPC-60-NH**₂ were collected using a Bruker Apex 2 Smart CCD surface detector at 150 K. The PXRD data were collected on a Panalytical X-Pert PRO diffractometer with Cu-Kα radiation. Elemental analyses (C, H, N) were performed using a CE instruments EA 1110 elemental analyzer. The 1H NMR spectrum was obtained using a 400 MHz Varian INOVA spectrometer. Thermo-gravimetric analysis (TGA) measurements were performed under N₂ atmosphere with a heating rate of 10°C min⁻¹ at the range of 40–900°C on a Mettler Toledo TGA instrument. Infrared spectra (IR) were obtained within the 400–4000 cm⁻¹ region on a Nicolet 330 FTIR Spectrometer. Gas adsorption experiments were carried out by using the surface area analyzer ASAP-2020. The UV-vis absorption spectrum were obtained on a 752 PC UV-vis spectrophotometer.

Synthesis of UPC-60-Cl [Fe₃O(L-Cl)₂(H₂O)₃]³H₂O

H₃L-Cl (7.0 mg, 0.023 mmol) and FeCl₃ (31.0 mg, 0.19 mmol) were ultrasonically dissolved in a mixed solvent of DMF (2 mL) and CH₃COOH (0.24 mL) in a 10 mL Teflon reactor. After slowly heated to 150°C in 1 h, the mixture was kept at 150°C for 12 h. Then the mixture was slowly cooled to 30°C at a rate of 0.1°C min⁻¹, and the dark-red crystals were collected, washed with DMF and then dried in air (yield: 65% based on H₃L-Cl). Elemental analysis calculated (%) for **UPC-60-Cl**: C, 37.82; H, 2.18. Found: C, 36.53; H, 2.11.

Synthesis of UPC-60-NH₂ [Fe₃O(L-NH₂)₂(H₂O)₃][.]4H₂O.

H₃L-NH₂ (15.0 mg, 0.054 mmol) and [Fe₃(μ ₃-O)(CH₃COO)₆] cluster^[55] (10.0 mg, 0.019 mmol) were ultrasonically dissolved in a mixed solvent of DMF (2 mL) and CH₃COOH (0.38 mL) in a 10 mL Teflon reactor. After slowly heated to 150°C in 1 h, the mixture was kept at 150°C for 12 h. Then the mixture was slowly cooled to 30°C at a rate of 0.1°C min⁻¹, and the dark-red crystals were collected, washed with DMF and then dried in air (yield: 67% based on H₃L-NH₂). Elemental analysis calculated (%) for **UPC-60-NH**₂: C, 39.60; H, 3.05; N, 3.55. Found: C, 39.52; H, 3.08; N, 3.56.

Crystal structure determinations

Crystallographic data of **UPC-60-CI** and **UPC-60-NH**₂ were collected by using Bruker Apex 2 Smart CCD surface detector at 150 K. Using an (Cu) X-ray source (Cu K α λ = 1.54184 Å) and a graphite monochromator were with Multiscan program SADABS for absorption correction. Structural analysis were performed by the Superflip method through the Olex 2 software package and the ShelXL method were used for structural refinement. All nonhydrogen atoms were anisotropically refined. The detailed crystallographic data for **UPC-60-CI** and **UPC-60-NH**₂ are listed in Supporting Information, respectively. Deposition numbers 2050509 (for **UPC-60-CI**) and 2051471 (for **UPC-60-NH**₂) contain the supplementary crystallographic data for this paper. These data are provided free of charge

by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Gas sorption measurements

The synthesized samples were washed with DMF three times, and then solvent-exchanged with methanol and dichloromethane three times, respectively. The activated samples were obtained by degassing at 120°C for 12 h under high vacuum. Gas adsorption experiments of N₂, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈, and CO₂ were carried out using an ASAP-2020 surface area analyzer. The pore distribution and Brunauer Emmett Teller (BET) specific surface area were calculated by using the N₂ adsorption isotherm at 77 K. The temperature of 77 K, 273 K and 298 K during the test were maintained by liquid nitrogen bath, ice water bath and normal temperature water bath, respectively.

Dye adsorption measurements

Five organic dyes (Rhodamine B (RHB), Crystal violet (CV), Xylenol orange (XO), Methyl orange (MO), and Chrome Blue K (CBK)) with different charges and sizes were used to test the adsorption capacity of the **UPC-60-CI** and **UPC-60-NH**₂. Before the adsorption, the synthesized samples were treated with activation as in the gas adsorption measurements process. For the maximum adsorption capacity, 10 mg samples were added to 10 mL different organic dye aqueous solutions with a concentration of 10-500 ppm and stirred continuously for 24 h. Then the liquid was centrifuged and the supernatant was taken and tested using the UV-vis spectrophotometer. The maximum adsorption capacity was calculated by the Langmuir model:

$$Qe = \frac{Ce}{Q_{max}} + \frac{1}{Q_{max} \cdot b}$$

(Ce (ppm): equilibrium concentration of dyes; Qe (mg g⁻¹): the adsorption amounts of dyes; Q_{max} : the maximum adsorption capacity of dyes; b: the Langmuir constant). In addition, 10 mg samples were added to 10 mL 20 ppm different organic dye aqueous solutions, the adsorption rate were obtained by testing the adsorption amount at different times.

Breakthrough experiments

Breakthrough experiments of equimolar C_2H_2/CO_2 mixed gases were completed employing a fixed bed. The **UPC-60-CI** (365.7 mg) and **UPC-60-NH₂** (362.2 mg) which solvent-exchanged with methanol and dichloromethane were filled in a stainless steel column respectively and then kept at 120°C for 12 h with the He flow (2 mL min⁻¹ at 298 K) for activation ahead of the experiment. After that, the column was filled with He flow, and the equimolar C_2H_2/CO_2 mixed gas was introduced to the column (2 mL min⁻¹ at 298 K).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (NSFC, Grant No. 21875285), the Fundamental Research Funds for the Central Universities (20CX05010A), and the Key Research and Development Projects of Shandong Province (2019JZZY010331).

 $\label{eq:keywords:Metal-Organic Frameworks \bullet Ligand Conformation \\ Regulation \bullet Dye Adsorption \bullet C_2H_2/CO_2 \ Separation \\ \end{array}$

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FULL PAPER

Entry for the Table of Contents

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Two 3D Fe-MOFs (UPC-60-CI and UPC-60-NH₂) were constructed based on UPC-200(Fe)-H-H₂O by replacing part of the benzene rings with C=C bonds and modifying -CI- and -NH₂ on the ligand. The synergistic effect of diversified structure and modification of functional groups endow UPC-60-CI and UPC-60-NH2 with high adsorption capacity for dyes and good C₂H₂/CO₂ separation ability. Through reasonable regulation of ligands with functional groups, the structure can be precisely regulated to achieve the adsorption and separation of specific guest molecules.



Metal–Organic Frameworks

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Optimizing Fe-based Metal-Organic Frameworks through Ligand Conformation Regulation for Efficient Dye Adsorption and C₂H₂/CO₂ Separation