The Selective CO$_2$ Adsorption and Photothermal Conversion Study of an Azo-Based Cobalt-MOF Material

Li-Long Dang $^{1,4}$, De-Xi Zong $^{2,4}$, Xiao-Yan Lu $^{1,©}$, Ting-Ting Zhang $^{1}$, Tian Chen $^{1}$, Jiu-Long Sun $^{1}$, Jiu-Zhou Zhao $^{1}$, Meng-Yang Liu $^{1}$ and Shui-Ren Liu $^{3,*}$

1 Henan Key Laboratory of Function-Oriented Porous Materials, College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471934, China
2 Hubei Nuclear Industry Geological Bureau, Xiaogan 432003, China
3 School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China
* Correspondence: lsrzdx@zzu.edu.cn
† These authors contributed equally to this work.

Abstract: A new metal–organic framework (MOF), [Co$_2$(L)$_2$(azpy)$_n$] (compound 1, H$_2$L = 5-(pyridin-4-ylmethoxy)-isophthalic acid, azpy = 4,4′-azopyridine), was synthesized by a solvothermal method and further characterized by elemental analysis, IR spectra, thermogravimetric analysis, single-crystal and powder X-ray diffraction. The X-ray single-crystal diffraction analysis for compound 1 indicated that two cis L$_2^{2−}$ ligands connected to two cobalt atoms resulted in a macrocycle structure. Through a series of adsorption tests, we found that compound 1 exhibited a high capacity of CO$_2$, and the adsorption capacity could reach 30.04 cm$^3$/g. More interestingly, under 273 K conditions, the adsorption of CO$_2$ was 41.33 cm$^3$/g. In addition, when the Co-MOF was irradiated by a 730 nm laser, rapid temperature increases for compound 1 were observed (temperature variation in 169 s: 26.6 °C), showing an obvious photothermal conversion performance. The photothermal conversion efficiency reached 20.3%, which might be due to the fact that the parallel arrangement of azo units inhibited non-radiative transition and promoted photothermal conversion. The study provides an efficient strategy for designing MOFs for the adsorption of CO$_2$ and with good photothermal conversion performance.

Keywords: metal–organic frameworks; porous material; crystal structure; CO$_2$ adsorption; photothermal conversion

1. Introduction

The emission of CO$_2$ will cause a rise in the global average temperature, which will lead to a series of ecological and environmental problems [1–4]. At present, there are two feasible methods for reducing CO$_2$ concentrations. One is to develop new sources of energy that can be recycled, and the other is to use CO$_2$ as a starting material to convert it into useful chemical products. However, disadvantages such as high cost and high energy consumption are the challenges in solving the above problems. Researchers have been trying to explore new recyclable adsorption materials for the adsorption and separation of CO$_2$. Metal–organic frameworks (MOFs) as functional materials, due to their ease of design, diverse structure, chemical modifiability, high porosity and specific surface area, have been widely investigated in various fields such as fluorescent sensing [5–12], heterogeneous catalysis [13–18], drug delivery [19–24], gas storage and separation [25–32]. Modifying the metal sites and organic ligands is conducive to improving the adsorption and separation ability of the materials [33–38].

To date, numerous MOFs have been designed for the adsorption and separation of CO$_2$ [39–45]. Luo et al. made many outstanding efforts in the field of gas adsorption [44–49]. For example, they designed a porous DMOF based on a photosensitive diarylethene ligand, and the photochromic behavior was controlled by UV irradiation with visible light for the
first time [50], with up to a 75% CO₂-desorption capacity. Additionally, they constructed another metal-organic framework material with a highly photosensitive structure by substituting diarylethene ligands for azo ligands, ECUT-15 [47]. Under UV irradiation, it still performed its general CO₂ adsorption capability and had a highly selective adsorption of CO₂ over N₂, CH₄, O₂ and CO. At instantaneous conditions, the CO₂ capture/release performance was up to 78%. In addition, M-MOF-74 series were reported by Matzger A. J. et al. and Long J. R. et al., respectively [51,52]. The results showed that M-MOF-74 had a highly selective adsorption capacity for CO₂ under low pressure conditions due to the strong coordination between the unsaturated metal ions and CO₂ in the structure. There is an increasing number of MOFs supplied for small molecule gas adsorption and purification. However, the development of this research remains quite slow.

In addition, photothermal therapy has been demonstrated to have potential for cancer treatment because of the forceful killing of diseased lesions with high selectivity under near-infrared laser irradiation [53,54]. Except for purely inorganic materials or purely organic materials displaying the function of converting NIR light to heat, MOFs have also shown effective photothermal conversion capacity, which has been demonstrated by various ruthenium MOFs and Zn-MOFs based on π–π stacking interactions [55,56]. Although a variety of MOF complexes with near-infrared photothermal conversion properties have been achieved, reports about the photothermal effects induced by conjugation effects based on azo bonds are rare.

Herein, we report a new cobalt-based MOF, compound 1, formulated as [Co₂(L)₂(azpy)]ₙ (H₂L = 5-(pyridin-4-ylmethoxy)-isophthalic acid, azpy = 4,4′-azopyridine), which was synthesized under solvothermal conditions, and its crystal structure was determined by single-crystal X-ray diffraction (Scheme 1). Compound 1 was characterized by the IR spectrum, elemental analysis, PXRD, solid-state UV–Vis absorption and thermogravimetric analysis. In addition, compound 1 exhibited a high selectivity for CO₂ under 273 K conditions. The adsorption capacity could reach 41.33 cm³/g. In addition, obvious photothermal conversion performance was observed under 730 nm laser irradiation accompanied by a high conversion efficiency of 20.3% (temperature change: 53.6 °C).

Scheme 1. Chemical structures of azpy and H₂L in this work.

2. Results

2.1. Crystal Structural Description

The single-crystal X-ray diffraction analysis indicated that compound 1 crystallized in a monoclinic P2₁/c space group. In the asymmetric unit (Figure 1), compound 1 contained two crystallographically independent Co(II) ions, namely Co1 and Co2 ions, and each Co²⁺ ion had a hexahedral coordination environment with four carboxylic oxygen atoms from three different H₂L ligands, one pyridine nitrogen atom from the azpy ligand and one pyridine nitrogen atom from the L²⁻ ligand in the opposite direction. Careful analyzing of this structure showed that a methylene group serving as a flexible site was present in the H₂L ligand, which caused the formation of a cage-type unit, in which the separation between two phenyl units was 6.92 Å. Furthermore, these cage-type units were bridged by multiple azpy ligands, finally resulting in the generation of a novel three-
dimensional framework structure. Notably, a very large pore structure was observed in this 3D framework, showing a \(6.3 \text{ Å} \times 11.7 \text{ Å}\) window. Platon calculated a solvent-accessible void space of 2042.1 Å\(^3\) (equal to 40.6% of the cell volume), showing the potential porous MOFs of compound 1. Moreover, the azpy ligands were arranged in parallel, in which the distance between two azo units was 3.42 Å, reflecting obvious \(\pi-\pi\) stacking interaction between the azpy ligands. In addition, an eight-membered ring was found based on two \(\text{cis} H_2L\) ligands by the connection of two cobalt atoms (Figure 2). Additionally, the bond lengths were \(\text{Co1} - \text{O1} = 2.088(2) \text{ Å}\), \(\text{Co1} - \text{O2} = 2.300(19) \text{ Å}\), \(\text{Co1} - \text{O5} = 1.998(19) \text{ Å}\), \(\text{Co1} - \text{O7} = 2.035(18) \text{ Å}\), \(\text{Co1} - \text{N5} = 2.182(3) \text{ Å}\) and \(\text{Co1} - \text{N6} = 2.148(3) \text{ Å}\). Furthermore, the adjacent non-bonding distance of Co1–Co2 was 4.35 Å.

![Figure 1](image1)

**Figure 1.** Single-crystal X-ray structure of 1. Coordination environment of Co\(^{2+}\) ions in 1 (a); coordination geometry of ligand \(L_2^{2-}\) (b); view of parallel arrangement mode of azpy in 1 (c); view of 2D structure of 1 (d).

![Figure 2](image2)

**Figure 2.** View of the 3D framework of compound 1.
2.2. PXRD and Thermal Properties

The simulated and experimental PXRD patterns of compound 1 are shown in Figure 3. Their peak positions corresponded well with each other, indicating the phase purity of the solids, although some small shifts were observed, which might be attributed to the cis–trans isomerism of the azo bonds [57,58].

![Figure 3](image-url)

Figure 3. The PXRD patterns of compound 1 (a); infrared spectroscopy (IR) of compound 1 (b).

In addition, the thermal stability of compound 1 was also investigated under a nitrogen atmosphere in the temperature range of 20–800 °C. From the TG curve (Figure 4), we found that the first weight loss occurred from 20 to 183 °C, which corresponded to the loss of the free water and DMF molecules. Additionally, there was almost no weight loss from 183 to 221 °C. Upon further heating above 221 °C, the successive losses corresponded to the collapse of the skeleton (352 °C) and the decomposition of the organic ligands (383 °C). In addition, the solid-state UV-Vis absorption of compound 1 was also explored carefully from 250 to 800 nm with a UV-vis spectrophotometer. The result clearly reflected a strong absorption from 300 to 550 nm. A careful structural analysis of this compound showed that the strong and wide-range UV-Vis absorption might be related to the absorption of azpy ligands due to the fact that the azo bond is a good chromophore, which can effectively absorb photoelectrons (Figure 4a) [9].

![Figure 4](image-url)

Figure 4. The solid-state UV–Vis absorption of compound 1, ligand azpy and H₃L (a); thermogravimetric curves of compound 1 (b).

2.3. Adsorption Properties

The high chemical stability and thermal stability of compound 1 prompted us to study the gas adsorption performances. As shown in Figure 5a,b, the porosity of the activated
The materials of compound 1 was manifested by N$_2$ adsorption at 77 K, expressing a fully reversible type-I isotherm, a signature characteristic of microporous materials, and giving a BET of 402.6 m$^2$/g, a uniform pore size of 1.0 nm and a total pore volume of 0.21 cm$^3$/g. Furthermore, this proper porosity and desirable aperture encouraged us to investigate the adsorption selectivity of CO$_2$/CH$_4$/CO in detail. At 298 K, the adsorption isotherms of the single components CO$_2$, CH$_4$ and CO were collected, as presented in Figure 6a. Compound 1 showed a unique adsorption capacity for CO$_2$ compared to CH$_4$ and CO. Furthermore, the adsorption amount of CO$_2$ (30.04 cm$^3$/g) was higher than that of CH$_4$ (8.71 cm$^3$/g) and CO (9.12 cm$^3$/g). Finally, we further explored the adsorption capacity of compound 1 of CO$_2$ under the influence of different temperatures (Figure 6b). The experimental results showed that the adsorption value could reach 41.33 cm$^3$/g at 273 K. All the above experimental studies indicated that compound 1 could be used as a potential adsorbing material for CO$_2$ in the future (Table 1).

Figure 5. The N$_2$ adsorption at 77 K of compound 1 (a); the distribution of pore size of compound 1 (b).

Figure 6. The adsorption isotherms of CO$_2$, CH$_4$ and CO for compound 1 (a); The adsorption isotherms of CO$_2$ at 273 K and 298 K for compound 1 (b).
Table 1. A comparison table indicating the CO$_2$ adsorption properties of several novel materials.

| MOF                 | Adsorption (CO$_2$) | Temperature | Ref (doi)                          |
|---------------------|---------------------|-------------|------------------------------------|
| ZSM-5               | 1.630 mmol/g        | 363 K       | J. Porous Mater. 2022, 29, 19.     |
| SBA-16              | 1.630 mmol/g        | 363 K       | J. Porous Mater. 2022, 29, 19.     |
| Zr$_3$(OH)(p-cdc)$_{2.5}$ | 0.586 mmol/g    | 298 K       | Sci. Total Environ. 2020, 707, 135090. |
| PEI-MCM-41          | 5.495 mmol/g        | 373 K       | doi:10.1080/09593330.2021.1958012. |
| HPS−PEHA-70         | 4.5 mmol/g          | 343 K       | Materials 2016, 9(10), 835.        |
| Cu-OATA             | 2.236 mmol/g        | 298 K       | ACS Appl. Mater. Interfaces 2021, 13, 33188. |
| Cd-OATA             | 0.509 mmol/g        | 298 K       | ACS Appl. Mater. Interfaces 2021, 13, 33188. |
| MOF-177             | 33.5 mmol/g         | 298.15 K    | Environ. Sci. Pollut. Res. 2019, 26, 36214. |
| Mg-MOF-74           | 3.7 mmol/g          | 77 K        | ACS. Omega 2021, 6, 7739.          |
| MCFs                | 0.45 mmol/g         | 77 K        | ACS. Omega 2021, 6, 7739.          |
| [{Co$_2$(2,6-NDC)$_2$(L)$_2$}·xG]$_n$ | 3.35 mmol/g  | 273 K       | Inorg. Chem. 2019, 58, 11553.      |
| [{Co$_2$(2,6-NDC)$_2$(L)$_2$}·xG]$_n$ | 2.70 mmol/g  | 295 K       | Inorg. Chem. 2019, 58, 11553.      |
| [Co$_x$(L)$_2$(azpy)]$_n$ | 1.845 mmol/g | 273 K       | This work                          |

2.4. Photothermal Conversion Properties

To our knowledge, π−π stacking interactions can trigger active non-radiative pathways and the inhibition of the radiative transition process, leading to an effective photothermal (PT) conversion phenomenon [59–63]. Furthermore, all the UV–vis spectra of compound 1 and two ligands displayed obvious near infrared absorption at 730 nm (Figure 4a). In addition, the TGA of compound 1 proved that compound 1 was able to maintain good structural stability until 221 °C, telling us that the temperature rise induced by the photothermal conversion was probably not the cause of the change in the structural framework (Figure 4b). Thus, the near-infrared photothermal conversion performance of compound 1 was performed earnestly under irradiation from a 730 nm near-infrared laser. In contrast, the temperature change experiments of the ligands H$_2$L and azpy were also explored carefully under the same conditions as that of compound 1.

Firstly, crystalline compound 1 was irradiated at a power of 0.6 W/cm$^2$ under a 730 nm laser accompanied by the conditions of the external temperature being stable. Interestingly, a rapid temperature rise was observed. The temperature rose to 75.0 °C from 21.4 °C in only 109 s. Once the 730 nm near-infrared laser was turned off, the temperature declining process was seen clearly by the infrared imaging camera, reflecting the good photothermal conversion properties of compound 1 (Figure 7). Thus, the near-infrared photothermal conversion efficiency of compound 1 was calculated based on the reduced temperature data according to the calculation method described below (Equations (1)–(4)), showing a high conversion efficiency of 20.3%, reflecting the excellent near-infrared photothermal performance of Co−MOF, i.e., compound 1. In contrast, illumination experiments of the ligands H$_2$L and azpy under a 730 nm laser were also carried out. The results showed that the temperature increase in the ligands H$_2$L and azpy was extremely weak and the temperature changes were 4.5 °C (from 22.1 to 26.6 °C) and 3.0 °C (from 22.4 to 25.4 °C), which was negligible (Figure 8). A careful analysis of structure 1 showed that the π−π stacking interaction between the azpy ligands could trigger non-radiative transition and induce obvious photothermal conversion effects.

Based on the total energy balance of the system:

\[
\sum_i m_i c_{pi} \frac{dT}{dt} = Q_s - Q_{loss} \tag{1}
\]

\[
\eta = hS \Delta T_{max}/I \left(1 - 10^{-A}\right) \tag{2}
\]
where \( h \) is the heat transfer coefficient and \( S \) is the surface area of the container. \( I \) is the laser power (0.6 W cm\(^{-2}\)). When the temperature reaches its maximum, the system is in equilibrium.

\[
Q_s = Q_{\text{loss}} = hS \Delta T_{\text{max}}
\]

where \( h \) is the heat transfer coefficient and \( S \) is the surface area of the container. \( I \) is the laser power (0.6 W cm\(^{-2}\)).

\[
\tau_s = \sum m_i c_{p,i} / hS, \quad \text{such that} \quad \frac{d\theta}{dt} = \frac{Q_s}{\tau_s hS \Delta T_{\text{max}}} - \frac{\theta}{\tau_s}, \quad \text{and when the laser is off,} \quad Q_s = 0,
\]

\[
\tau_s = -1 / \ln \theta. \quad \text{The value of} \quad \tau_s \quad \text{was obtained from the cooling curve of sample. The photothermal conversion efficiency} \quad \eta \quad \text{was 20.3%}.
\]

**Figure 7.** (a) Photothermal conversion images of compound 1 and ligands H\(_2\)L and azpy; (b) Diagram of photothermal conversion measurement.

**Figure 8.** (a) Photothermal conversion curve of compound 1 and ligands azpy and H\(_2\)L; (b) fitting the linear line of ln\(\theta \)– t in the solid state of compound 1 under laser irradiation of 0.6 W/cm\(^2\).

### 3. Experiment

#### 3.1. Materials and Methods

All reagents and solvents were analytical grade and were obtained from commercial sources and used without further purification. Elemental analyses (C, H and N) were performed on a Vario EL III elemental analyzer. The infrared spectrum was measured with KBr pellets in the 4000–400 cm\(^{-1}\) region on a Nicolet 170SX spectrometer. Thermogravimetric analyses were performed on an SDT 2960 thermal analyzer from room temperature to 800 \(^\circ\)C at a heating rate of 20 K min\(^{-1}\) under nitrogen flow. Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/MAX-2500PC diffractometer with Cu/K\(_\alpha\) radiation (\(\lambda = 1.5406 \, \text{Å}\)) over a 2\(\theta\) range of 5–50\(^\circ\) with a scan speed of 5\(^\circ\)/min at room temperature.
CO₂ (99.99%), N₂ (99.99%), CH₄ (99.99%) and CO (99.99%) gas adsorption measurements were performed using an ASAP 2020 system. UV-visible absorption spectra were recorded on a Lambda 750 s UV-vis spectrophotometer.

3.2. Synthesis of Compound 1

A mixture of H₂L (27 mg, 0.10 mmol), azpy (18 mg, 0.10 mmol) and Co(NO₃)₂·6H₂O (29 mg, 0.10 mmol) were dissolved in DMF (6 mL) and H₂O (2 mL) in a screw-capped vial. The vial was capped and heated at 100 ℃ for 72 h. Orange block crystals of 1 were obtained in high yields (92%) based on the H₂L ligand. Elemental analysis was calculated (%) for 1 C₃₈H₂₆Co₂N₆O₁₀ (844.52): C, 54.04; H, 3.10; N, 9.95. It was found as: C, 54.07; H, 3.11; N, 9.50. The IR for 1 was: 3397 m, br, 3075 m, 2929 m, 2353 w, 1666 m, 1569 s, 1394 s, 1250 m, 1117 w, 1057 w, 920 vs, 845 w, 782 m, 727 m, 673 vs, 622 vs, 567 s, 528 vs, 479 vs.

3.3. Single-Crystal X-ray Structure Determination

The single-crystal X-ray diffraction analysis of 1 was carried out on a Rigaku Saturn 724 CCD diffractometer (Mo-Kα, λ = 0.71073 Å) at room temperature. The structure was solved by a direct method with SHELXS-97 [64] and refined by the full-matrix least-squares method on F² with anisotropic displacement parameters for all non-H atoms (SHELXL-97) [65]. An empirical absorption correction was applied by the SADABS program [66]. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement with the use of geometrical restraints. The crystallographic data and selected bond lengths and angles for 1 are listed in Table 2.

### Table 2. Crystallographic data and experimental details for compound 1.

| Complex | 1 |
|---------|---|
| Empirical formula | C₃₈H₂₆Co₂N₆O₁₀·3[H₂O] |
| Formula weight | 898.55 |
| Temperature/K | 293(2) |
| Crystal system | monoclinic |
| Space group | P2₁/c |
| a/Å | 20.0316(9) |
| b/Å | 16.1623(5) |
| c/Å | 15.9700(6) |
| α/° | 90 |
| β/° | 103.454(5) |
| γ/° | 90 |
| Volume/Å³ | 5028.5(3) |
| Z | 4 |
| ρ calc / g cm⁻³ | 1.187 |
| μ / mm⁻¹ | 0.717 |
| F(000)/e | 1840.0 |
| 2θ range for data collection/° | 6.584 to 50.054 |
| Reflections collected | 22293 |
| Independent reflections | 8824 [R int = 0.0404, R sigma = 0.0615] |
| Data/restraints/parameters | 8824/0/505 |
| Goodness-of-fit on F² | 1.029 |
| Largest diff. peak/hole, e Å⁻³ | 0.35/−0.38 |
| Final R indexes [I> 2σ(I)] | R₁ = 0.0481, wR₂ = 0.1098 |
| Final R indexes [all data] | R₁ = 0.0662, wR₂ = 0.1182 |

Crystallographic data for the structural analysis were deposited at the Cambridge Crystallographic Data Center, and CCDC No. 2,178,932 for compound 1 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) (accessed on 10 September 2022).
4. Conclusions

To conclude, we indeed constructed a new cobalt-based MOF [Co$_2$(L)$_2$(azpy)]$_n$ ($\text{H}_2$L = 5-(pyridin-4-ylmethoxy)-isophthalic acid, azpy = 4,4'-azopyridine) by a solvothermal method. Notably, compound 1 had relative high CO$_2$ adsorption capacities, namely 30.04 cm$^3$/g and 41.33 cm$^3$/g at 298 K and 273 K, respectively. However, the adsorption capacity of other gases was very weak (CH$_4$: 8.71 cm$^3$/g and CO: 9.12 cm$^3$/g). Interestingly, compound 1 showed a rapid temperature change from 20.4 to 47.0 °C under a 730 nm laser radiation and the photothermal conversion efficiency could reach 20.6%, reflecting the good photothermal conversion properties of compound 1. This study will promote the development of new photothermal conversion materials and gas adsorption materials.

Author Contributions: L.-L.D. and D.-X.Z.: synthesis of the title complex, formal analysis, IR-related experiment. L.-D.: writing—review and editing. T.-T.Z. and T.C.: completed cultivation and testing of single crystals. J.-L.S. and J.-Z.Z.: completed formal analysis and gas adsorption. X.-Y.L. and M.-Y.L.: completed UV–Vis absorption spectra and photothermal conversion experiment. S.-R.L.: supervision, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Natural Science Foundation of Henan Province (No. 212300410209), Key Scientific Research Projects of Higher Education of He’nan Province (Grant 22A150016), the Shanghai Science and Technology Committee (19DZ2270100) and Heluo Young Talent Lifting Project (2022HLTJZC09).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Fan, Y.L.; Zhang, H.P.; Yin, M.J.; Krishna, R.; Feng, X.F.; Wang, L.; Luo, M.B.; Luo, F. High adsorption capacity and selectivity of SO$_2$ over CO$_2$ in a metal–organic framework. Inorg. Chem. 2021, 60, 4–8. [CrossRef] [PubMed]
2. Gu, S.F.; Xiong, X.H.; Gong, L.L.; Zhang, H.P.; Xu, Y.; Feng, X.F.; Luo, F. Classified encapsulation of an organic dye and metal–organic complex in different molecular compartments for white-light emission and selective adsorption of C$_2$H$_2$ over CO$_2$. Inorg. Chem. 2021, 60, 8211–8217. [CrossRef] [PubMed]
3. Belmabkhout, Y.; Bhatt, P.M.; Adil, K.; Pillai, R.S.; Cadiau, A.; Shkurenko, A.; Maurin, G.; Liu, G.; Koros, W.J.; Eddaoudi, M. Natural gas upgrading using a fluorinated MOF with tuned H$_2$S and CO$_2$ adsorption selectivity. Nat. Energy 2018, 3, 1059–1066. [CrossRef]
4. Qin, J.H.; Xiao, Z.; Xu, P.; Li, Z.H.; Lu, X.Y.; Yang, X.G.; Lu, W.W.; Ma, L.F.; Li, D.S. Anionic porous Zn-Metalated porphyrin metal–organic framework with PtS topology for gas-phase photocatalytic CO$_2$ reduction. Inorg. Chem. 2022, 61, 13234–13238. [CrossRef] [PubMed]
5. Sun, T.Y.; Gao, Y.B.; Du, Y.Y.; Zhou, L.; Chen, X. Recent advances in developing lanthanide metal–organic frameworks for ratiometric fluorescent sensing. Front. Chem. 2020, 8, 624592. [CrossRef]
6. Liu, X.J.; Zhang, Y.H.; Chang, Z.; Li, A.L.; Tian, D.; Yao, Z.Q.; Jia, Y.Y.; Bu, X.H. A water-stable metal–organic framework with a double-helical structure for fluorescent sensing. Inorg. Chem. 2016, 55, 7326–7328. [CrossRef]
7. Li, Y.L.; Zhao, Y.; Wang, P.; Kang, Y.S.; Liu, Q.; Zhang, X.D.; Sun, W.Y. Multifunctional metal–organic frameworks with fluorescent sensing and selective adsorption properties. Inorg. Chem. 2016, 55, 11821–11830. [CrossRef]
8. Liu, X.B.; Lin, H.; Xiao, Z.Y.; Fan, W.D.; Huang, A.; Wang, R.M.; Zhang, L.L.; Sun, D.F. Multifunctional lanthanide–organic frameworks for fluorescent sensing, gas separation and catalysis. Dalton Trans. 2016, 45, 3743–3749. [CrossRef]
9. Li, T.; Dang, L.; Zhao, C.; Lv, Z.; Yang, X.; Zhao, Y.; Zhang, S. A self-sensitized Co (II)-MOF for efficient visible-light-driven hydrogen evolution without additional cocatalysts. J. Solid State Chem. 2021, 304, 122609–122614. [CrossRef]
10. Qin, J.; Xu, P.; Huang, Y.; Xiao, L.; Lu, W.; Yang, X.; Ma, L.; Zang, S. High loading of Mn(II)-metalated porphyrin in MOF for photocatalytic CO$_2$ reduction in gas–solid condition. Chem. Commun. 2021, 57, 8468–8471. [CrossRef]
11. Qin, J.-H.; Qin, W.-J.; Xiao, Z.; Yang, J.-K.; Wang, H.-R.; Yang, X.-G.; Li, D.-S.; Ma, L.-F. Efficient energy-transfer-induced high photoelectric conversion in a dye-encapsulated ionic pyrene-based metal–organic framework. Inorg. Chem. 2021, 60, 18593–18597. [CrossRef] [PubMed]
12. Chang, X.H.; Qin, J.H.; Han, M.L.; Ma, L.F.; Wang, L.Y. Exploring the structural diversities and magnetic properties of copper(II) and manganese(II) complexes based on 5-methoxysalicylate and flexible bis (imidazole) ligands. *CrystEngComm* **2014**, *16*, 870–882. [CrossRef]

13. Zhou, Z.; Wang, Y.; Peng, F.; Meng, F.; Zha, J.J.; Ma, L.; Du, Y.H.; Peng, N.; Ma, L.F.; Zhang, Q.H.; et al. Intercalation-activated layered MoO3 nanobelts as biodegradable nanozymes for tumor-specific photo-enhanced catalytic therapy. *Angew. Chem. Int. Ed.* **2021**, *61*, e202115939.

14. Yang, X.G.; Zhai, Z.M.; Lu, X.M.; Ma, L.F.; Yan, D.P. Fast crystallization-deposition of orderly molecule level heterojunction thin films showing tunable up-conversion and ultrahigh photoelectric response. *ACS Cent. Sci.* **2020**, *6*, 1169–1178. [CrossRef]

15. Yang, X.G.; Qin, J.H.; Huang, Y.D.; Zhai, Z.M.; Ma, L.F.; Yan, D.P. Highly enhanced UV-vis-NIR light harvesting and photoelectric conversion of pyrene MOF by encapsulation of D-α-cyanine dye. *J. Mater. Chem. C* **2020**, *8*, 17169–17175. [CrossRef]

16. Chang, X.H.; Zhao, Y.; Han, M.L.; Ma, L.F.; Wang, L.Y. Five Cd(II) coordination polymers based on 2,3′,5,5′-biphenyltetracarboxylic acid and N-donor ligand: Syntheses, structures and fluorescent properties. *CrystEngComm* **2014**, *16*, 6417–6424. [CrossRef]

17. Chang, X.H.; Qin, W.J.; Zhang, X.Y.; Jin, X.; Yang, X.G.; Dou, C.X.; Ma, L.F. Angle-Dependent Polarized Emission and Photoelectron Performance of Dye-Encapsulated Metal-Organic Framework. *Inorg. Chem.* **2021**, *60*, 10109–10113. [CrossRef]

18. Yang, X.; Zhai, Z.; Lu, X.; Qin, J.; Li, F.; Ma, L. Hexanuclear Zn(II)-Induced Dense π-Stacking in a Metal–Organic Framework Featuring Long-Lasting Room Temperature Phosphorescence. *Inorg. Chem. 2020*, *59*, 10395–10399. [CrossRef]

19. Yang, X.G.; Lu, X.M.; Zhai, Z.M.; Zhao, Y.; Li, F.; Ma, L. π-Type halogen bonding enhanced the long-lasting room temperature phosphorescence of Zn(ii) coordination polymers for photoelectron response applications. *Inorg. Chem. Front.* **2020**, *7*, 2224–2230. [CrossRef]

20. Zhang, H.P.; Gong, L.L.; Yin, M.J.; Xiong, X.H.; Zhang, Q.Y.; Feng, X.F.; Luo, F.; Carney, J.B.; Yue, Y.F. Efficient organic iodide capture by a mesoporous bimetallic-organic framework. *Cell Rep. Phys. Sci.* **2022**, *3*, 100830. [CrossRef]

21. Yang, X.G.; Lu, X.M.; Zhai, Z.M.; Zhao, Y.; Liu, X.Y.; Ma, L.F.; Zang, S.Q. Facile synthesis of micro-scale MOF host-guest with long-last phosphorescence and enhanced optoelectronic performance. *Chem. Commun.* **2019**, *55*, 11099–11102. [CrossRef] [PubMed]

22. Qin, J.; Zhang, H.; Sun, P.; Huang, Y.; Shen, Q.; Yang, X.; Ma, L. Ionic liquid induced highly dense assembly of porphyrin in MOF nanosheets for photovoltaic energy conversion. *Dalton Trans.* **2020**, *49*, 17772–17778. [CrossRef] [PubMed]

23. Zhao, Y.; Yang, X.; Lu, X.; Yang, C.; Fan, N.; Yang, Z.; Wang, L.; Ma, L. [Zn6] cluster based metal-organic framework with enhanced room-temperature phosphorescence and optoelectronic performances. *Inorg. Chem. 2019*, *58*, 6215–6221. [CrossRef] [PubMed]

24. Dang, L.; Li, T.; Cui, Z.; Sui, D.; Ma, L.; Jin, G. Selective construction and stability studies of molecular trefoil knot and solomon link. *Dalton Trans.* **2021**, *50*, 16984–16989. [CrossRef] [PubMed]

25. Wang, Y.; Yang, G.P.; Zhang, P.F.; Ma, L.L.; Wang, J.M.; Li, G.P.; Wang, Y.Y. Microporous Cd(II) Metal–Organic Framework for CO2 Catalysis, Luminescent Sensing, and Absorption of Methyl Green. *Cryst. Growth Des.* **2021**, *21*, 2734–2743. [CrossRef]

26. Liu, J.; Hang, M.; Wu, D.; Jin, J.; Cheng, J.G.; Yang, G.P.; Wang, Y.Y. Fine-tuning the porosities of the entangled isostructural Zn(II)-based metal–organic frameworks with active sites by introducing different N-auxiliary ligands: Selective gas sorption and efficient CO2 conversion. *Inorg. Chem. 2020*, *59*, 2450–2457. [CrossRef] [PubMed]

27. Xue, D.X.; Wang, Q.; Bai, J.F. Amide-functionalized metal–organic frameworks: Syntheses, structures and improved gas storage and separation properties. *Coord. Chem. Rev.* **2019**, *378*, 2–16. [CrossRef]

28. Dang, L.; Li, T.; Zhao, C.; Zhang, T.; Ye, X.; Sun, X.; Wang, H.; Ma, L. Supramolecular Rh6 catalytic system promoting directed [4+4] cycloaddition reaction of anthracene under UV irradiation. *J. Solid State Chem.* **2022**, *306*, 122785–122792. [CrossRef]

29. Li, J.; Xiong, L.; Fu, L.; Bo, W.; Du, Z.; Feng, X. Structural diversity of Mn(II) and Cu(II) complexes based on 2-carboxyphenoxyacetate linker: Syntheses, conformation comparison and magnetic properties. *J. Solid State Chem.* **2022**, *305*, 122636. [CrossRef]

30. Li, J.; Zhang, Y.; Du, Z.; Feng, X. One-pot solvothermol synthesis of mononuclear and oxalate-bridged binuclear nickel compounds: Structural analyses, conformation alteration and magnetic properties. *Inorg. Chem. Acta* **2022**, *530*, 120697. [CrossRef]

31. Daglar, H.; Gulbaskan, H.C.; Avci, G.; Aksu, G.O.; Altundal, O.F.; Altintas, C.; Ercu, I.; Keskin, S. Effect of metal–organic framework (MOF) database selection on the assessment of gas storage and separation potentials of mofs. *Angew. Chem. Int. Ed.* **2021**, *60*, 7828–7837. [CrossRef] [PubMed]

32. Dhainaut, J.; Bonneau, M.; Ueoka, R.; Kanamori, K.; Furukawa, S. Formulation of metal–organic framework inks for the 3D printing of robust microporous solids toward high-pressure gas storage and separation. *ACS Appl. Mater. Interfaces* **2020**, *12*, 10983–10992. [CrossRef] [PubMed]

33. Li, J.R.; Sculley, J.; Zhou, H.C. Metal–organic frameworks for separations. *Chem. Rev.* **2012**, *112*, 869–932. [CrossRef] [PubMed]

34. Zhang, J.P.; Zhang, Y.B.; Lin, J.B.; Chen, X.M. Metal azolate frameworks: From crystal engineering to functional materials. *Chem. Rev.* **2012**, *112*, 1001–1033. [CrossRef] [PubMed]

35. Wang, H.R.; Yang, X.G.; Qin, J.H.; Ma, L.F. Long-lived room temperature phosphorescence of organic–inorganic hybrid systems. *Inorg. Chem. Front.* **2021**, *8*, 1942–1950. [CrossRef]

36. Wang, H.; Meng, W.; Wu, J.; Ding, J.; Hou, H.; Fan, Y. Crystalline central-metal transformation in metal-organic frameworks. *Coord. Chem. Rev.* **2016**, *307*, 130–146. [CrossRef]
37. Wang, L.L.; Li, T.T.; Zhang, T.T.; Zhao, Y.; Chen, T.; Gao, X.; Ma, L.F.; Jin, G.X. Highly selective synthesis and near-infrared photothermal conversion of metallia-Borromean ring and [2]catenane assemblies. *Chem. Sci.* 2022, 13, 5130–5140. [CrossRef]

38. Wang, Y.F.; Li, S.H.; Ma, L.F.; Geng, J.I.; Wang, L.Y. Syntheses, crystal structures, and magnetic studies of two cobalt(II) coordination polymers based on concurrent ligand extension. *Inorg. Chem. Commun.* 2015, 62, 42–46. [CrossRef]

39. Liu, X.T.; Jia, Y.Y.; Zhang, Y.H.; Ren, G.I.; Feng, R.; Zhang, S.Y.; Zaworotko, M.J.; Bu, X.H. A new Co(II) metal–organic framework with enhanced CO2 adsorption and separation performance. *Inorg. Chem. Front.* 2016, 3, 1510–1515. [CrossRef]

40. Pal, A.; Chand, S.; Das, M.C. A water-stable twofold interpenetrating microporous MOF for selective CO2 adsorption and separation. *Inorg. Chem. Front.* 2017, 56, 13991–13997. [CrossRef]

41. Yuan, J.Q.; Li, J.T.; Che, S.T.; Li, G.H.; Liu, X.Y.; Sun, X.D.; Zou, L.F.; Zhang, L.R.; Liu, Y.L. Two unique copper cluster-based metal–organic frameworks with high performance for CO2 adsorption and separation. *Inorg. Chem. Front.* 2019, 6, 556–561. [CrossRef]

42. Dang, L.L.; Zhang, T.T.; Chen, T.; Zhao, Y.; Zhao, C.C.; Aznarez, F.; Sun, K.X.; Ma, L.F. Coordination assembly and NIR photothermal conversion of Cp*Rh-based supramolecular topologies based on distinct conjugated systems. *Org. Chem. Front.* 2022, 9, 5505–5515. [CrossRef]

43. Dang, L.L.; Chen, T.; Zhang, T.T.; Li, T.T.; Sun, J.L.; Zhang, K.J.; Ma, L.F. Size-induced highly selective synthesis of organometallic rectangular macrocycles and heterometallic cage based on half-sandwich rhodium building block. *Molecules* 2022, 27, 3756. [CrossRef] [PubMed]

44. Guo, L.J.; Feng, X.F.; Gao, Z.; Krishna, R.; Luo, F. Robust 4d–5f bimetal–organic framework for efficient removal of trace SO2 from SOx/COx/NOx/N2 mixtures. *Inorg. Chem.* 2021, 60, 1310–1314. [CrossRef]

45. Fan, C.B.; Gong, L.L.; Huang, L.; Luo, F.; Krishna, R.; Yi, X.F.; Zheng, A.M.; Zhang, L.; Pu, S.Z.; Feng, X.F.; et al. Significant enhancement of C2H2/C2H4 separation by a photochromic diarylethenene unit: A temperature- and Light-Responsive separation switch. *Angew. Chem. Int. Ed.* 2020, 59, 7900–7906. [CrossRef]

46. Xu, Z.Z.; Xiong, X.H.; Xiong, J.B.; Krishna, R.; Li, L.B.; Fan, Y.L.; Luo, F.; Chen, B.L. A robust Th-azole framework for highly efficient purification of C2H4 from a C2H2/C2H2/C2H4 mixture. *Nat. Commun.* 2020, 11, 3163. [CrossRef]

47. Luo, F.; Fan, C.B.; Luo, M.B.; Wu, X.L.; Zhu, Y.; Pu, S.Z.; Xu, W.Y.; Guo, G.C. Photoswitching CO2 capture and release in a photochromic diarylethene metal–organic framework. *Angew. Chem. Int. Ed.* 2014, 53, 9298–9301. [CrossRef]

48. Dang, L.L.; Zhang, T.T.; Li, T.T.; Chen, T.; Zhao, Y.; Zhao, C.C.; Ma, L.F. Stable Zinc-Based Metal–Organic Framework Photocatalyst for Effective Visible-Light-Driven Hydrogen Production. *Molecules* 2022, 27, 1917. [CrossRef]

49. Pei, X.R.; Dang, L.L.; Zhang, T.T.; Chen, T.; Ren, F.X.; Liu, S.R. Stable nickel-based metal–organic framework containing thiophene/diimidazole units for effective near-infrared photothermal conversion. *Catalysis* 2022, 12, 777. [CrossRef]

50. Caskey, S.R.; Wong-Foy, A.G.; Matzger, A.J. Dramatic tuning of carbon dioxide uptake via metal substitution in a coordination polymer with cylindrical pores. *J. Am. Chem. Soc.* 2008, 130, 10870–10871. [CrossRef]

51. Wang, H.; Qin, J.; Huang, C.; Han, Y.; Xu, W.; Hou, H. Mono/bimetallic water-stable lanthanide coordination polymers as luminescent probes for detecting cations, anions and organic solvent molecules. *Dalton Trans.* 2016, 45, 12710–12716. [CrossRef]

52. Mason, J.A.; Sumida, K.; Herm, Z.R.; Krishna, R.; Long, J.R. Evaluating metal–organic frameworks for post-combustion carbon dioxide capture via temperature swing adsorption. *Energy Environ. Sci.* 2011, 4, 3030–3040. [CrossRef]

53. Lyu, Y.; Fang, Y.; Miao, Q.Q.; Zhen, X.; Ding, D.; Pu, K.Y. Intraparticle molecular orbital engineering of semiconducting polymer nanoparticles as amplified theranostics for in vivo photoacoustic imaging and photothermal therapy. *ACS Nano* 2016, 10, 4472–4481. [CrossRef] [PubMed]

54. Pu, K.; Shuhendler, A.J.; Juckerst, J.V.; Mei, J.G.; Gambhir, S.S.; Bao, Z.N.; Rao, J.H. Semiconducting polymer nanoparticles as photacoustic imaging probes in living mice. *Nat. Nanotechnol.* 2014, 9, 233–239. [CrossRef] [PubMed]

55. Yan, T.; Li, Y.Y.; Gu, Q.Y.; Li, J.; Su, J.; Wang, H.Y.; Zuo, J.L. A Tetrathiafulvalene/Naphthalene Diimide-Containing Metal–Organic Framework with fsc Topology for Highly Efficient Near-Infrared Photothermal Conversion. *Inorg. Chem. Front.* 2021, 8, 3078–3085. [CrossRef]

56. Liu, Y.G.; Liu, G.L.; Peng, T.; Gu, C.; Gu, C.; Li, J.J.; Liu, X.Q.; Sun, L.B. Near-infrared light triggered release of ethane from a photothermal metal-organic framework. *Chem. Eng. J.* 2021, 420, 130490. [CrossRef]

57. Lyndon, R.; Konstas, K.; Ladewig, B.P.; Southon, P.D.; Kept, C.J.; Hill, M.R. Dynamic photo-switching in metal–organic frameworks as a route to low-energy carbon dioxide capture and release. *Angew. Chem. Int. Ed.* 2013, 52, 3695–3698. [CrossRef]

58. Chen, B.L.; Ma, S.Q.; Eric, J.; Hurtado, E.J.; Lobkovsky, E.B.; Zhou, H.C. A triply interpenetrated microporous metal–organic framework for selective sorption of gas molecules. *Inorg. Chem.* 2007, 46, 8490–8492. [CrossRef]

59. Yu, W.; Qu, F.-Y.; Luo, S.-T.; Shi, H.-T.; Yuan, G.; Wei, X. Coordination Assembly and Host-Guest Chemistry of a triply Interlocked [2]Catenane. *Inorg. Chem. Front.* 2021, 8, 2356–2364. [CrossRef]

60. Gao, X.; Cui, Z.; Shen, Y.-R.; Liu, D.; Lin, Y.-J.; Jin, G.-X. Synthesis and near-infrared photothermal conversion of discrete supramolecular topologies featuring half-sandwich [Cp*Rh] Units. *J. Am. Chem. Soc.* 2021, 143, 17833–17842. [CrossRef]

61. Wang, Y.; Zhu, W.; Du, W.; Liu, X.; Zhang, X.; Dong, H.; Hu, W. Cocrystals strategy towards materials for near-infrared photothermal conversion and imaging. *Angew. Chem. Int. Ed.* 2018, 57, 3963–3967. [CrossRef]

62. Liu, J.C.; Wang, J.F.; Han, Q.; Guan, P.S.; Liu, L.L.; Chen, L.J.; Zhao, J.W.; Streib, C.; Song, Y.F. Multicomponent self-assembly of a giant heterometallic polyanionoxtungstate supercluster with antitumor activity. *Angew. Chem. Int. Ed.* 2021, 60, 11153–11157. [CrossRef] [PubMed]
63. Zhou, Z.; Li, X.Q.; Hu, T.T.; Xue, B.L.; Chen, H.; Ma, L.F.; Liang, R.Z.; Tan, C.L. Molybdenum-Based Nanomaterials for Photothermal Cancer Therapy. Adv. NanoBiom Res. 2022. [CrossRef]

64. Sheldrick, G.M. SHELXS-97, Program for the Solution of Crystal Structure; University of Göttingen: Göttingen, Germany, 1997.

65. Sheldrick, G.M. SHELXL-97, Program for the Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.

66. Sheldrick, G.M. SADABS Siemens Area Correction Absorption Program; University of Göttingen: Göttingen, Germany, 1994.