Peer Review File

Manuscript Title: Carbon dioxide capture from open air using covalent organic frameworks

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referees' comments:

Referee #1 (Remarks to the Author):

Zihui Zhou et al. report the CO2 capture from ambient air using a polyamine-functionalized covalent organic framework. CO2 capture from air is becoming increasingly important as it becomes more and more obvious that we will not be able to phase out fossil fuels quickly enough to reduce global warming to reasonable levels. The post-synthetically modified COF has a CO2 capacity of about 2 mmol g-1 in humid air and can release the captured CO2 upon heating to 60-100 °C.
Overall, I think this is a convincing study. The materials are well characterized and their performance and stability are documented. After 20 days and 100 CO2 adsorption / desorption cycles in air the CO2 uptake performance is virtually unchanged. The topic as well as the results presented here are scientifically and technologically important and are expected to be of high interest to the broad readership of Nature. I recommend the publication of this study after the following points have been addressed.

1. The authors show that the affinity of the functionalized COF towards CO2 is high (which is of course good and required) and attribute this to the formation of carbamates when humidity is present. However, this chemical trapping of CO2 will come at the expense of higher energy required for desorption. The authors use temperatures of 60-100 °C to release the adsorbed CO2. What I think would be important to add here is how much energy is required to capture the CO2 from air and how this compares to other technologies.

2. The authors give a very brief account of other technologies for direct air capture in the introduction. I think it would be good to add a comparison of the state of the art technologies with their respective performance characteristics to the SI, including the capture capacity and energy requirements. This would allow the reader to better understand the performance of the new COF.

Referee #2 (Remarks to the Author):

General Comment
Even though several direct air capture technology has reached pilot scale demonstrations the application of COF is very few. It is great to see that reticular chemistry and name reaction have been applied to enhance the stability of direct air capture adsorbent. The research has carried out 100 cycles of studies to prove the stability of the adsorbent under atmospheric conditions. The COF-999 adsorbent was characterized by various instrument and the crystal structure of COF-999 was

modeled. The DAC properties of this newly synthesized COF outperformed previously studied organic covalent framework. Therefore the decision is a minor revision.
Minor Comment：
1) In the abstract the author wrote “a durable material.... has not been developed”. This is not quit the case for direct air capture technology now. Some solid amines, ion exchange resins as well as MOFs have reached pilot demonstrations. The abstract should probably keep the background within research covalent organic framework and how the research has made this class of material suitable for DAC.
2) Please provide reasoning for a relatively low CO2 capacity of COF-999 under dry conditions.
3) What is the largest reaction scale possible to prepare this adsorbent?

Referee #3 (Remarks to the Author):

This work, a very good read, covers an interesting, extensive study on a particular COF, which is part of a provisional patent application, starting from a facile synthetic scheme, and a detailed material characterization, including an extensive gas adsorptions study and a test for CO2 adsorption in open air. Overall the work is solid and theoretical support is provided where possible (e.g. XRD and adsorption structures). Below several recommendations are given. The main point of improvement – and this may also touch upon the topic of novelty, in the sense whether it merits publication in Nature or possible one of the other journals in the Nature Portfolio Group – relates to be more transparent to the current state-of-art, both in the introduction as well as the data interpretation.

Immediate interest to materials science community is justified and given the topic of COF adsorption this can be extended to other disciplines as well. In short: conceptually very interesting, but actual impact of the work – and I realize developments go step by step and often gradually – will largely depend on items that have been addressed in the outlook: scalability and implementation in an adsorption technique/device is yet to be explored.

Figure 2 contains a detailed set of XRD, gas adsorption and NMR analyses. The observations have been described clearly and compared theory (in the case of XRD) in a solid way and several, useful NMR modes have been utilized (further supported with additional data, e.g. IR and BET elsewhere in the paper/SI). However, the assignments/results and interpretations have not been linked with existing literature. Comparisons with literature are lacking. In the outlook the author present COF-999 as the new standard, but how about the current state-of-the-art on this? There is quite a number of references I could list here, see e.g. Chem. Soc. Rev., 2023, 52, 6294.

Also, can the observed average of 4.6 CH2CH2NH units per amine group be rationalized in terms of the numbers of amines groups per pore and the pore size (3.3 nm for COF-999-N3)?

The effect functionalization, i.e. the reduction of azides to amines, on the COF characteristics has been analyzed. How about all these characteristics upon the ROP of aziridine (e.g. surface area, pore size)?

Figure 3 contains a detailed set of XRD, gas adsorption and NMR analyses. The observations have been described clearly and compared theory (in the case of XRD) in a solid way and several, useful NMR modes have been utilized. However, the assignments/results and interpretations have not been linked with existing literature, with the exception of lines 172-174 (refs 27 and 28) and later, when studied the adsorption structures, line 230 (refs 29 and 30).

The T-dependent desorption data made me initially wonder whether the authors also thought about T-dependent adsorption data, allowing Arrhenius analysis. Later I bumped into Figure S9, so there may be an opportunity here to get additional thermodynamical data in the CO2-COF interactions.

Figure 4 covers the open air data, which contributes a lot to the originality and especially the impact of the work. Regarding these data and the study in general, all remarks related to 'retention' or 'full retention' are based on gas adsorption experiments. This look good indeed, but how about all other material properties?

What I miss in the introduction of the work is some (COF-related) background on the use of amines and CO2 interactions. The choice of using hydrophobic units is motivated will (lines 52-54, refs 21-23), previous amine-functionalized COF work has not properly been acknowledged in sentence of lines 54-57. The current text may suggest that the combination of amines and COFs i.r.t. CO2 adsorption is new and this can be fixed easily. Also, currently, references to other ways installing amines in COFs (e.g. ligand exchange) are lacking. In other words, the second DAC/COF challenge is poorly linked to existing work.

Please comments on the TGA results (Fig S13): how to explain the difference between the non-functionalized COF and (N3/NH2) functionalized COFs?

In general, the reporting of data and methodology seems sufficiently detailed and transparent to enable others reproducing the results. However, to what extend can the author comments on the reproducibility and repeatability? For example: Fig 3 is fine in terms of materials characterization, what is the accuracy of the BET and pore size (for different batches/syntheses)? How about the gas adsorption data, particularly Fig 3e? Accuracy on these particular results is not clear.

Lastly, two minor points. First, the authors used the word series, while in this work one COF has been made (and functionalized and tested). While this COF and related chemistry, including possible variation of the building blocks, can indeed be seen as an example that representation a larger platform, I suggest the authors use the series more exclusively for appropriate cases.

Second, realizing that authors can chose any label they want for a certain material or sample and also realizing that COF names/numbering is arbitrary, the term COF-999 does raise a question: the number 999 has been chosen because it looks and reads nice or is there any logic?

Author Rebuttals to Initial Comments:

Referee #1 (Remarks to the Author):

Zihui Zhou et al. report the CO_2 capture from ambient air using a polyamine-functionalized covalent organic framework. CO_2 capture from air is becoming increasingly important as it becomes more and more obvious that we will not be able to phase out fossil fuels quickly enough to reduce global warming to reasonable levels. The post-synthetically modified COF has a CO_2 capacity of about 2 mmol g^{-1} in humid air and can release the captured CO_2 upon heating to 60-100 °C.

Overall, I think this is a convincing study. The materials are well characterized and their performance and stability are documented. After 20 days and 100 CO_2 adsorption / desorption cycles in air the CO_2 uptake performance is virtually unchanged. The topic as well as the results presented here are scientifically and technologically important and are expected to be of high interest to the broad readership of Nature. I recommend the publication of this study after the following points have been addressed.

Response: We thank the referee for the positive evaluation and strong recommendation of our work.

1. The authors show that the affinity of the functionalized COF towards CO_2 is high (which is of course good and required) and attribute this to the formation of carbamates when humidity is present. However, this chemical trapping of CO_2 will come at the expense of higher energy required for desorption. The authors use temperatures of 60-100 °C to release the adsorbed CO_2. What I think would be important to add here is how much energy is required to capture the CO_2 from air and how this compares to other technologies.

Response: In the calculation of energy, water-carbamate hydrogen bonding and water desorption are the major contributors to consider. To address the referee's question, we used the following equations, which are typically used for the estimation of energy (references 34 and 35 in the supplementary information).

$$Q_{sens} = \left(C_{p,CO2} + \frac{q_{H2O}}{q_{CO2}} C_{p,H2O} + \frac{1}{q_{CO2}} C_{p,sorbent}\right) \times (T_{des} - T_{ads})$$

$$Q_{des} = \Delta H_{CO2} + \frac{q_{H2O}}{q_{CO2}} \Delta H_{H2O} + \Delta H_{H-bond}$$

Where Q_{sens} is the sorbent's sensible heat and Q_{des} is the desorption enthalpy. The physical properties used in the calculation are as follows:

Physical properties	Values
Heat capacity of sorbent, $C_{p,sorbent}$	1.5[a] kJ kg^{-1} K^{-1}
Heat capacity of CO_2, $C_{p,CO2}$	0.85 kJ kg^{-1} K^{-1}
Heat capacity of water, $C_{p,H2O}$	4.18 kJ kg^{-1} K^{-1}
Heat of adsorption of CO_2[b], ΔH_{CO2}	53 kJ mol^{-1}
Heat of adsorption of water[b], ΔH_{H2O}	49 kJ mol^{-1}

Heat of hydrogen bond dissociation[c], ΔH_{H-bond}	49 kJ mol^{-1}
$T_{des} - T_{ads}$	35 °C
Water and CO_2 capacity ratio[d], q_{H2O}/q_{CO2}	2.5

a, Estimated from similar structures (reference 36 in the Supplementary information).
b, Isosteric heat of adsorption, calculated from the Clausius-Clapeyron equation (Supplementary Figs. 6 and 8).
c, Estimated from DFT calculation (Section 14), the difference between the CW1 and CA1 energies corresponds to the sum of the total energy to the dissociation of multiple hydrogen bonds.
d, Calculated from water (5.0 mmol g^{-1}) and CO_2 (2.0 mmol g^{-1}) capacities under 400 ppm CO_2 and 50% RH.

From these data, COF-999 requires a total heat of 259 kJ mol^{-1} (including 34 kJ mol^{-1} sensible heat and 225 kJ mol^{-1} desorption enthalpy) for desorption under 60 °C after the adsorption from 400 ppm CO_2 and 50% RH. The materials reported in the literature use a desorption temperature of 100 °C or higher instead of the lower temperature of 60 °C needed for desorption in our case. Thus, to make a comparison, we recalculated our energetics at 100 °C, and the comparison of the literature is as follows: the state-of-the-art solid amine sorbents require a sensible heat of 73 kJ mol^{-1}, and a total energy of 298 kJ mol^{-1}. Other reported solid-supported amines are also usually more hydrophilic and take up water to CO_2 in a 4 to 12 ratio (reference 34 in the supplementary information), leading to a total energy requirement of 336 to 749 kJ mol^{-1} if desorbed under 60 °C. From the calculation, the energy requirements for COF-999 are significantly lower than those of other sorbents.

We added the calculation above as Supplementary Information section 12 (page 42 in supplementary information) and referred to it in the main text:

[Revised Manuscript Line 187] *"The hydrophobic nature of COF-999 allows CO_2 desorption with lower energy input for the removal of water molecules (Supplementary Information section 12), thereby resulting in a low desorption temperature and fast desorption kinetics."*

Furthermore, we include an extensive table comparing the energetics and other parameters for a wide range of materials, including traditional hydroxides and amine liquids, in Supplementary Table 2 (page 7 in supplementary information).

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Response: This is an excellent suggestion for which we added Supplementary Tables 1 and 2 (on pages 6 and 7 in supplementary information), as explained at the end of the previous response. In addition, we have modified the manuscript as follows:

[Revised Manuscript Line 37] *"Extensive research has been reported for using liquid alkaline solutions[6,7], silica-supported amines[8–10], and metal-organic frameworks (MOFs)[11–15] as potential candidates for DAC applications (see Supplementary Tables 1 and 2 for more details)."*

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General Comment

Even though several direct air capture technology has reached pilot scale demonstrations the application of COF is very few. It is great to see that reticular chemistry and name reaction have been applied to enhance the stability of direct air capture adsorbent. The research has carried out 100 cycles of studies to prove the stability of the adsorbent under atmospheric conditions. The COF-999 adsorbent was characterized by various instrument and the crystal structure of COF-999 was modeled. The DAC properties of this newly synthesized COF outperformed previously studied organic covalent framework. Therefore the decision is a minor revision.

Response: We thank the referee for the positive evaluation of our work and are pleased that the referee appreciates the performance of COFs for DAC applications.

Minor Comment:

1) In the abstract the author wrote "a durable material.... has not been developed". This is not quit the case for direct air capture technology now. Some solid amines, ion exchange resins as well as MOFs have reached pilot demonstrations. The abstract should probably keep the background within research covalent organic framework and how the research has made this class of material suitable for DAC.

Response: We have modified the statement by replacing "…has not been developed" to "…remains underdeveloped". This more accurately reflects the need for durable materials for DAC.

2) Please provide reasoning for a relatively low CO_2 capacity of COF-999 under dry conditions.

Response: The relatively lower CO_2 capacity under dry conditions compared to humid conditions can be explained by the fact that under dry conditions, the formation of only carbamic acid is favored, while under humid conditions, two additional species (carbamate and bicarbonate) contribute to the uptake by increasing the amine efficiency. This was fully discussed in the "Adsorption Structures of CO_2 in COF-999" section of the original manuscript, and we kept it in the revised manuscript (line 231 to 254).

3) What is the largest reaction scale possible to prepare this adsorbent?

Response: In this study, we optimized the synthetic conditions of COF-999 at a scale of ~ 50 mg per reaction to achieve optimal performance of CO_2 capacity. This performance is maintained at the gram scale, and we are in the process of optimizing for the kilogram scale. However, such scale-up will take some time and will hopefully be reported in the future.

Referee #3 (Remarks to the Author):

This work, a very good read, covers an interesting, extensive study on a particular COF, which is part of a provisional patent application, starting from a facile synthetic scheme, and a detailed material characterization, including an extensive gas adsorptions study and a test for CO_2 adsorption in open air. Overall the work is solid and theoretical support is provided where possible (e.g. XRD and adsorption structures). Below several recommendations are given. The main point of improvement – and this may also touch upon the topic of novelty, in the sense whether it merits publication in Nature or possible one of the other journals in the Nature Portfolio Group – relates to be more transparent to the current state-of-art, both in the introduction as well as the data interpretation.

Immediate interest to materials science community is justified and given the topic of COF adsorption this can be extended to other disciplines as well. In short: conceptually very interesting, but actual impact of the work – and I realize developments go step by step and often gradually – will largely depend on items that have been addressed in the outlook: scalability and implementation in an adsorption technique/device is yet to be explored.

Response: We thank the referee for making insightful suggestions to clarify and improve the content overall.

We appreciate the referee's comments and points of view. The object of this work is to show that COFs, a robust class of porous materials, can serve as exceptional DAC materials. The list of state-of-the-art materials and their performances included in the newly added Supplementary Table 1 shows how COFs exceed many classes in performance and, indeed, rival if not exceed other materials in the most important requirement of material to be practical for DAC. We showed for the first time that a DAC material can be cycled 100 times in the open-air cycling CO_2 without degradation. This finding makes COFs stand out from other materials. For the sake of clarity, we added Supplementary Table 1 which is in agreement with what we state in the main text of the revised manuscript.

Figure 2 contains a detailed set of XRD, gas adsorption and NMR analyses. The observations have been described clearly and compared theory (in the case of XRD) in a solid way and several, useful NMR modes have been utilized (further supported with additional data, e.g. IR and BET elsewhere in the paper/SI). However, the assignments/results and interpretations have not been linked with existing literature. Comparisons with literature are lacking.

Response: To link our data processing and interpretation with existing literature, we added three new citations and edited some current citations in the manuscript.

[PXRD, line 85, ref 27] *"Pawley refinement[27] was conducted with the experimental PXRD …"*

[BET, line 93. ref 28] *" … , giving a Brunauer-Emmett-Teller (BET) surface area[28] of 811…"*

[NMR, line 104, ref 30] *"… characteristic R–$^{15}NH_2$ chemical shift[30] at 23.5 ppm in ^{15}N ssNMR …"*

[IR, line 105, ref 29] *" …of vibrational absorbance bands at 2089 cm^{-1} for azide $\nu_{N=N}$ stretch[29] …"*

[NMR, line 110, ref 30] *"… which was assigned to the formation of secondary amines[30] …"*

[Breakthrough, line 154, ref 31] *" The sharp breakthrough curve suggests the rapid mass transfer of CO_2 in COF-999.[31]"*

References for this response:
27. Pawley, G. S. Unit-cell refinement from powder diffraction scans. *J. Appl. Crystallogr.* **14**, 357–361 (1981).
28. Brunauer, S., Emmett, P. H. & Teller, E. Adsorption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.* **60**, 309–319 (1938).
29. Ji, W. *et al.* Removal of GenX and perfluorinated alkyl substances from water by amine-functionalized covalent organic frameworks. *J. Am. Chem. Soc.* **140**, 12677–12681 (2018).
30. Mao, H. *et al.* A scalable solid-state nanoporous network with atomic-level interaction design for carbon dioxide capture. *Sci. Adv.* **8**, eabo6849 (2022).
31. McCabe, W. L., Smith, J. C. & Harriott P. *Unit Operations of Chemical Engineering, 7th Edition*. (McGraw Hill, 2004)

In the outlook the author present COF-999 as the new standard, but how about the current state-of-the-art on this? There is quite a number of references I could list here, see e.g. Chem. Soc. Rev., 2023, 52, 6294.

Response: To compare COF-999 with current state-of-the-art materials, we added a summary of selected state-of-the-art sorbents in Supplementary Table 1 and referred to it in the manuscript:

[Revised Manuscript Line 37] *"Extensive research has been reported for using liquid alkaline solutions[6,7], silica-supported amines[8–10], and metal-organic frameworks (MOFs)[11–15] as potential candidates for DAC applications (see Supplementary Tables 1 and 2 for more details)."*

Regarding the reference mentioned by the reviewer (*Chem. Soc. Rev.* 2023, **52**, 6294, now cited as reference 21 in the revised manuscript), most of the previously reported COFs focus on the physisorption of CO_2 and are not able to adsorb CO_2 under low pressure (400 ppm). To acknowledge previous COFs, we added the sentence below in the introduction:

[Revised Manuscript Line 42] *"Employing the design principles of reticular chemistry[19,20], amine-functionalized[21] covalent organic frameworks (COFs) were synthesized to increase CO_2 physisorption affinity for the separation of CO_2 from gas mixtures (typical CO_2 concentration > 10%). However, to capture CO_2 directly from the air under practical conditions, it is essential to incorporate stronger chemisorption sites[4,22] in a more stable backbone."*

Also, can the observed average of 4.6 CH_2CH_2NH units per amine group be rationalized in terms of the numbers of amines groups per pore and the pore size (3.3 nm for COF-999-N3)?

Response: The average of 4.6 CH_2CH_2NH units can be rationalized. On average, each layer of hexagonal COF pore contains about 24 amines, as shown in the crystal model of COF-999 (see the CIF file attached). From the model, there is sufficient pore space in the pore to accommodate 24 amines. On the other hand, during the polymerization reaction, there needs to be enough space for the diffusion of the monomer (aziridine), catalyst (acetic acid), and solvent (toluene).

Consequently, the pore space cannot be fully occupied by CH_2CH_2NH units, leading to the reaction being limited to an average of 4.6 units per amine group.

The effect functionalization, i.e. the reduction of azides to amines, on the COF characteristics has been analyzed. How about all these characteristics upon the ROP of aziridine (e.g. surface area, pore size)?

Response: In the revised version of supplementary information, we further calculated the surface area and pore size of COF-999. After the ring-opening polymerization (ROP) of aziridine, COF-999 exhibited a BET surface area of 24 $m^2\ g^{-1}$ and a pore size of 1.4 nm (see updated Supplementary Fig. 4 on page 11 of Supplementary Information), which are smaller than those of the COF before the loading of polyamine (COF-999-NH_2, 881 $m^2\ g^{-1}$, 3.3 nm). The reductions in surface area and pore size are also evidence of successful polyamine loading inside the COF pores.

Figure 3 contains a detailed set of XRD, gas adsorption and NMR analyses. The observations have been described clearly and compared theory (in the case of XRD) in a solid way and several, useful NMR modes have been utilized. However, the assignments/results and interpretations have not been linked with existing literature, with the exception of lines 172-174 (refs 27 and 28) and later, when studied the adsorption structures, line 230 (refs 29 and 30).

Response: We have edited our reference list to link our data assignments and interpretation with existing literature, and we have revised the manuscript in a similar way to the question discussed immediately above.

The T-dependent desorption data made me initially wonder whether the authors also thought about T-dependent adsorption data, allowing Arrhenius analysis. Later I bumped into Figure S9, so there may be an opportunity here to get additional thermodynamical data in the CO_2-COF interactions.

Response: This was included in the original supplementary information in Supplementary Figs. 6 and 8. As correctly pointed out by the reviewer, the temperature-dependent CO_2 and water isotherms allow us to analyze their heat of adsorption in COF-999. We utilized the Clausius-Clapeyron equation (two-point form of Arrhenius equation) to calculate the heat of adsorption of CO_2 and water from temperature-dependent isotherm data, and the results have been shown in Supplementary Figs. 6 and 8, where Q_{st} (CO_2) = 53 kJ mol^{-1} and Q_{st} (H_2O) = 49 kJ mol^{-1}, respectively.

Figure 4 covers the open air data, which contributes a lot to the originality and especially the impact of the work. Regarding these data and the study in general, all remarks related to 'retention' or 'full retention' are based on gas adsorption experiments. This look good indeed, but how about all other material properties?

Response: To address this suggestion, we further confirmed the retention of atom connectivity and morphology of the material. FT-IR and SEM imaging were used to characterize the COF-999

sample after the open-air cycling experiment, where no change was observed after 100 cycles. We added the new FT-IR and SEM results in the Supplementary Figs. 1 and 10 (page 8 and 17 in supplementary information) and referred to them in the main text:

[Revised Manuscript Line 227] *"We further measured single-component CO_2 sorption isotherm (Fig. 4c), dynamic breakthrough using simulated air (400 ppm of CO_2 with 50% RH) (Fig. 4d), FT-IR (Supplementary Fig. 10), and SEM (Supplementary Fig. 1) of COF-999 after the completion of the 100 adsorption-desorption cycles. No changes in sorption isotherm, breakthrough, FT-IR, or SEM were observed, indicating retention of the COF structure and its proper functioning in CO_2 capture."*

What I miss in the introduction of the work is some (COF-related) background on the use of amines and CO_2 interactions. The choice of using hydrophobic units is motivated will (lines 52-54, refs 21-23), previous amine-functionalized COF work has not properly been acknowledged in sentence of lines 54-57. The current text may suggest that the combination of amines and COFs i.r.t. CO_2 adsorption is new and this can be fixed easily. Also, currently, references to other ways installing amines in COFs (e.g. ligand exchange) are lacking. In other words, the second DAC/COF challenge is poorly linked to existing work.

Response: Regarding the COF-related background on the use of amines and CO_2 interactions, in this work, we focus on COFs for direct air CO_2 capture. There are very few reported amine-functionalized COFs for DAC applications, and we have cited the first COF for DAC application as ref 22 in line 55.

We proposed our strategy in the second DAC/COF challenge: adding a covalently bonded initiator to the COF and conducting its polymerization to polyamines to allow the covalent bonding of polyamines. Previous DAC materials were unable to achieve both high amine loading (high uptake) and covalent bonding (high stability). Our strategy aims to overcome this challenge, differing from previously reported amine-functionalized COFs, such as those using ligand exchange. Among the previously reported amine-COF combinations, we think the most related literature is the Staudinger reaction in COFs, which we have cited as ref 29 in line 97.

We would like to emphasize that most previously reported amine-COF combinations have focused on CO_2 separation or capture under higher pressures. However, this manuscript focuses on COFs for direct air CO_2 capture. To further compare and acknowledge the previous work on amine-COF interactions, we added the following sentence in the introduction:

[Revised Manuscript Line 42] *"Employing the design principles of reticular chemistry[19,20], amine-functionalized[21] covalent organic frameworks (COFs) were synthesized to increase CO_2 physisorption affinity for the separation of CO_2 from gas mixtures (typical CO_2 concentration > 10%). However, to capture CO_2 directly from the air under practical conditions, it is essential to incorporate stronger chemisorption sites[4,22] in a more stable backbone."*

Please comments on the TGA results (Fig S13): how to explain the difference between the non-functionalized COF and (N_3/NH_2) functionalized COFs?

Response: We added a detailed explanation of the TGA results in the supplementary information (on page 26), and it is attached below:

COF-999-N_3 exhibited 3 major steps of weight loss, including desorption of adsorbed molecules (25–50 °C, 1.4 wt. %), decomposition of azides (200–315 °C, 7.9 wt.), and decomposition of the framework (315–800 °C, 43.9 wt. %).

COF-999-NH_2 exhibited 2 major steps of weight loss, including desorption of adsorbed molecules (25–50 °C, 1.4 wt. %) and decomposition of the framework (250–800 °C, 48.0 wt. %).

COF-999 exhibited 2 major steps of weight loss, including desorption of adsorbed molecules (25–65 °C, 6.0 wt. %) and decomposition of the framework (250–800 °C, 75.2 wt. %).

In COF-999, a larger initial weight loss was observed from 25 to 65 °C, which can be attributed to the higher CO_2 capacity. The temperature of weight loss also matches the desorption temperature of CO_2.

The backbone of all three COFs began to decompose at 250 °C, however, the decomposition process of COF-999 occurred more rapidly. This rapid decomposition can be attributed to the steric repulsion of the added polyamine groups, which weakens the interlayer interactions and forces the layers apart under high temperatures (reference 30 in supplementary information).

At 800 °C, COF-999 also exhibited greater weight loss compared to the other two COFs. This can be attributed to two factors: (i) The polyethyleneimine chain in COF-999 would be completely decomposed under high temperature hence resulting in more weight loss (reference 31 in supplementary information), and (ii) the basicity of the polyamine could influence the thermostability of the COF backbone, leading to more complete decomposition of COF backbone when exposed to high temperatures. This has also been observed in other amine-functionalized COFs (reference 32 in supplementary information).

In general, the reporting of data and methodology seems sufficiently detailed and transparent to enable others reproducing the results. However, to what extend can the author comments on the reproducibility and repeatability? For example: Fig 3 is fine in terms of materials characterization, what is the accuracy of the BET and pore size (for different batches/syntheses)? How about the gas adsorption data, particularly Fig 3e? Accuracy on these particular results is not clear.

Response: In response to the referee's suggestion, we have remeasured N_2 sorption using different batches of COF to obtain BET and pore size information, which agrees with what we reported in the original manuscript. For the BET surface area and the pore size distribution, we added two more sorption datasets from different batches for each COF reported in the revised supplementary information to show the reproducibility (see updated Supplementary Figs. 2 to 4 on supplementary information page 9).

As for the dataset presented in Fig. 3e, which is the gas sorption data under different relative humidity, we remeasured two additional times for each data point (raw data shown in

Supplementary Fig. 17 on Supplementary Information page 33), and the results agree with what we reported in the original manuscript. We added error bars in the figure to show the accuracy of the dataset and revised the manuscript as follows:

[Revised Manuscript Line 159] *"Under dry conditions with 400 ppm of CO_2, COF-999 exhibited a CO_2 uptake of 0.96 (±0.03) mmol g^{-1}, which is comparable to its single-component CO_2 sorption result. When 25% RH was introduced into the measurement, the CO_2 adsorption capacity of COF-999 increased to 1.69 (±0.08) mmol g^{-1}. A further increase to 2.05 (±0.03) mmol g^{-1} in the capacity was observed upon increasing RH to 50%. This is a remarkable 2.14-fold increase in CO_2 capacity over the dry condition. A maximum capacity of 2.09 (±0.03) mmol g^{-1} is achieved at RH of 75%."*

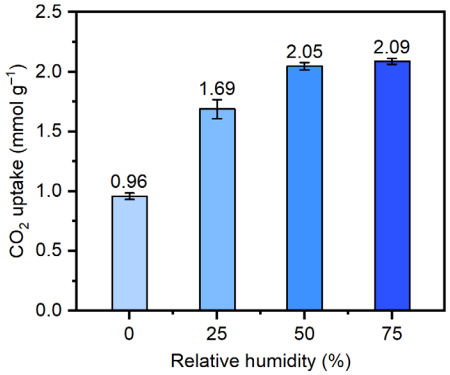

Fig. 3 | Thermodynamic and kinetic gas sorption studies of COF-999. *... **e**, CO_2 uptake under 400 ppm of CO_2 with 0, 25, 50, and 75% RH. Data shown are statistical averages and error bars represent one standard deviation. ...*

Lastly, two minor points. First, the authors used the word series, while in this work one COF has been made (and functionalized and tested). While this COF and related chemistry, including possible variation of the building blocks, can indeed be seen as an example that representation a larger platform, I suggest the authors use the series more exclusively for appropriate cases.

Response: We included in the paper a formula that gives the building block abbreviations and their molar ratios as labels of the COF compounds. Since these abbreviations are placed under a structural formula, they are appropriate for use as is typical in COF papers.

Second, realizing that authors can chose any label they want for a certain material or sample and also realizing that COF names/numbering is arbitrary, the term COF-999 does raise a question: the number 999 has been chosen because it looks and reads nice or is there any logic?

Response: Concerning the numbering of the COFs, in general, the numbers are roughly in chronological order of reporting. We have already reported COFs as high as 807, and we felt that this would be in line with the prevailing numbering scheme. Perhaps this naming scheme is clumsy, but it seems to have taken over the naming of frameworks ranging from zeolites to MOFs and now to COFs. The specific number of 999 is easy to remember. We hope that this is agreeable with the scientific community.

Reviewer Reports on the First Revision:

Referee #1 (Remarks to the Author):

Zihui Zhou et al. report the CO2 capture from ambient air using a polyamine-functionalized covalent organic framework. CO2 capture from air is becoming increasingly important as it becomes more and more obvious that we will not be able to phase out fossil fuels quickly enough to reduce global warming to reasonable levels. The post-synthetically modified COF has a CO2 capacity of about 2 mmol g-1 in humid air and can release the captured CO2 upon heating to 60-100 °C.

My concerns regarding the original submission were about the missing comparison with other established and evolving DAC technologies and the open questions about the energy required per ton of captured CO2. These points have now been addressed. I think the comparison tables in section 3 are helpful and sufficiently detailed but I recommend to add COF999 to supplementary table 2, even though its regeneration energy is calculated and not yet experimentally confirmed.

The calculation of the desorption energy is sufficiently detailed, confirming the excellent performance of the COF999 material and its potential for application.

Overall, I think the revised manuscript is a convincing study and I recommend its publication.

Referee #2 (Remarks to the Author):

The authors have clear addresses all the questions from the previous review.

Referee #3 (Remarks to the Author):

Overall, the authors have satisfactorily considered and addresses the point raised by the three reviewers. Appropriate changes, improvements actually, have been made.

*Summary of the key results
=> Remained the same, and this is fine.
*Originality and significance: if not novel, please include reference
=> My feedback on this topic has been dealt with properly.
*Data & methodology: validity of approach, quality of data, quality of presentation
=> The added analyses references to existing data have improved the work. Sorry that I missed the heat of adsorption data initially. I agree with the two-point form of Arrhenius equation; I was initially after a more elaborated analysis, but I have the feeling this approach suffices for now.
*Appropriate use of statistics and treatment of uncertainties
=>My feedback on this topic has been dealt with properly.
*Conclusions: robustness, validity, reliability
=> I agreed with the reply of the authors and the change/improvements/clarities made.

*Suggested improvements: experiments, data for possible revision
=> The authors have dealt with this properly. Given the current state of the work, I have not further suggestions.
*References: appropriate credit to previous work?
=> This improved as well, satisfactorily.
*Clarity and context: lucidity of abstract/summary, appropriateness of abstract, introduction and conclusions
=> Good.

Author Rebuttals to First Revision:

Referee #1 (Remarks to the Author):

Zihui Zhou et al. report the CO_2 capture from ambient air using a polyamine-functionalized covalent organic framework. CO_2 capture from air is becoming increasingly important as it becomes more and more obvious that we will not be able to phase out fossil fuels quickly enough to reduce global warming to reasonable levels. The post-synthetically modified COF has a CO_2 capacity of about 2 mmol g^{-1} in humid air and can release the captured CO_2 upon heating to 60-100 °C.

My concerns regarding the original submission were about the missing comparison with other established and evolving DAC technologies and the open questions about the energy required per ton of captured CO_2. These points have now been addressed. I think the comparison tables in section 3 are helpful and sufficiently detailed but I recommend to add COF999 to supplementary table 2, even though its regeneration energy is calculated and not yet experimentally confirmed.

The calculation of the desorption energy is sufficiently detailed, confirming the excellent performance of the COF999 material and its potential for application.

Overall, I think the revised manuscript is a convincing study and I recommend its publication.

Response: We thank the referee for the positive evaluation and strong recommendation of our work. We have added the calculated desorption energy of COF-999 in Supplementary Table 2.

Referee #2 (Remarks to the Author):

The authors have clear addresses all the questions from the previous review.

Response: We appreciate the referee's positive feedback and strong recommendation of our work.

Referee #3 (Remarks to the Author):

Overall, the authors have satisfactorily considered and addresses the point raised by the three reviewers. Appropriate changes, improvements actually, have been made.

*Summary of the key results

=> Remained the same, and this is fine.

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Response: We appreciate the referee's positive feedback and strong recommendation of our work.