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Peer Review File

A van der Waals porous crystal featuring conformational flexibility and permanent porosity for ultrafast water release

Corresponding Author: Professor Hiroshi Yamagishi

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I have reviewed the manuscript entitled "Molecular crystal with permanent and transformative porosity sustained thoroughly by van der Waals interactions for ultrafast water release" by Yamagishi and coworkers. The work describes the formation of a porous material that is assembled via van der Waals interactions. The porous material is able to adsorb water into the pores and be released by irradiation. Even under sealed conditions, the porous material is able to exert a considerable amount of force by releasing the pressure of the adsorbed water.

I think the manuscript is very well written and the work is convincing. I don't believe further experiments are necessary and the conclusions are supported by the data. My primary comments are in the introduction and are likely more stylistic than scientific.

Despite this, I'm not sure that this manuscript is a good fit for Communications Chemistry. As the authors clearly point out, this material has already been shown "slight spectral changes as a function of humidity". As such, I feel that this work is a good follow up but perhaps doesn't fit into the category of "Publishing significant advances across all areas of chemistry". I don't know that this work would influence the thinking in the field (especially given that the material is already known and would have made its impact from the previous publication).

Some general comments follow:
a) Page 4 the authors mention "Reticular bonding network together with flexible linkers and deformable bonds". As a porous materials person, I'm not sure I could define reticular bonding.

b) the authors state that "porous van der Waals crystals ... have been beyond the scope of crystal engineering because the conventional reticular bonding strategy is unapplicable". Again, it's not clear to me what reticular bonding is, and it's not clear to me that van der Waals materials could have them. Furthermore, I'm not sure that it's true that something is beyond the scope of crystal engineering. I think we haven't come up with design principles for it yet, and I'm not sure this work introduces those critical design elements for others to work from. I just know that this molecule works.

c) Similar to point b, "hardly designable" seems a bit harsh given that I'm not sure that this molecule was designed (or at least it's not clear to me from this manuscript that this molecule was designed for this outcome).

d) "to our knowledge" should be removed. Every word we write is "to our knowledge".

e) I think it's interesting that this is a polar spacegroup.

f) the authors state "for porous crystals since the kinetics dominates the separation efficiency". It's not clear to me why this would be true. Given large enough pores, thermodynamics would dominate separation efficiency. I don't know that there is a lot of data out there to support where kinetic separation stops and thermodynamic separation starts (with regards to pore aperture size or other functional components of the pores).

g) I'm not sure that I can reproduce the adsorption data. The experimental is not well defined other than the instrument used (and I admit that I am not familiar with that instrument) but kinetic data is not often something that a static adsorption instrument can produce. Also, any adsorption data should be reported in an AIF file for others to be able to examine (similar to any CIF file).

Reviewer #2

(Remarks to the Author)
Yamagishi and co-workers present a high quality investigation in which they illustrate a van der Waals crystal applied to ultrafast water release.

As the computational reviewer, I will defer comments on the synthesis and characterization to my reviewer colleagues and focus on the computation. The computation in this manuscript consists
of simulation of the IR spectrum as they key dihedrals change. This is completed using an appropriate computational method and I have no problems with the calculations that were done.
I do think, that the authors, particularly with their stated aims of designability, could do a lot more with their calculations, that would lend a lot of support both to the arguments in this manuscript and the future work of these authors and others.
Simple calculations that would increase the impact of the manuscript:
Energy of pi-pi stacking calculated from a dimer - both under vacuum and hydrated.
Inter-column interactions (i.e. interactions between molecules in the ab and ac directions) - either a dimer calculation using DFT and/or a semi-empirical calculation (DFTB) of a whole column.
Interaction energy of water in each identified binding site.
Potential energy surface (i.e. scan) of the highlighted dihedral angles - and then link this back to the pi-pi stacking energy above
A defect calculation (i.e. take the crystal structure and do a single point calculation after subtracting one molecule:
deltaE(defect) = E(crystal) - [E(crystal - molecule) + E(molecule)]

Line 244: For ease of navigation, please mention the section of the SI where the details can be found.

Reviewer #3

(Remarks to the Author)
K. Maejima et al report the water adsorption behavior on porous organic crystals. The observed adsorption behavior sounds interesting. However, the adsorption behavior is not necessarily well understood, even though authors assisted the fast water adsorption on their molecular crystals. The paper must be revised for publication.

1, Water adsorption on the sample crystals is the most key in the paper. The most important point is not necessarily quantitatively described. The water adsorption isotherm must be measured after the optimum preheating. The pore volumes assessable to N2 at 77 K and water at 298 K (room temp) can give the quantitative discussion. As water easily condenses on the sites at lower temperature in the adsorption system, quite accurate temperature control is requested. Then, authors can discuss how much pore spaces are occupied by N2 at 77 K and water at 298 K, giving the fractional filling using the pore volume derived from XRD and the observed adsorption amounts using the liquid density of N2 and water at adsorption temperature. Authors mention that their crystals can adsorb very rapidly H2O. However, this is not clearly shown, as given in 4.

The followings are minor comments.
2. 120 page 6: The samples are not sufficiently pre-treated. Authors may clarify the residual water in the crystals. The optimum preheating conditions must be determined. The strong adsorption sites such as crystal defects and chemical sites may be shown. The irreversibility must be qualitatively described.
3. 144 page 8: Could you show the reason why authors use “less affinitive to H2O ” instead of hydrophobic ?
Why the less-affinitive pores accelerate the transportation of water inside the pores?
4. 148-150 page 8: Authors assist that their crystals can quickly adsorb water compared with other porous materials. This comparative discussion is quite insufficient.
For example, authors mention the adsorption time on their crystals is about a half of that on activated carbon. There are so many kinds of activated carbons. If authors use high surface area activated carbons having many surface functional groups should show much shorter time. Then, “faster” is not evident. The more rigorous comparison should be necessary.
Also, zeolites show attractive water adsorption behavior and then the adsorption rate of several zeolites may be measured for the comparison, too.
5. 156 page 8: Can you remove the residual water by IR laser irradiation?
6. 156-157 page 8: Did you examine the possibility of the crystal degradation during
the IR laser irradiation? Can you describe the temperature change on the irradiation?

7. 162 page 8: Water vapor condenses easily on the sites having a lower temperature. Authors may show the uniformity of the temperature on measuring. The temperature must be controlled within ± 0.05 K at least.6.
8.183-185 page 10: Authors can explain the relationship between adsorption and molecular motion more precisely.
9. 189 page 10: Could you discuss on the effect of IR-excitation on water adsorption?
10. page11: Could you discuss on the effect of visible-light irradiation on water adsorption?
Is there any structural change in the pore walls?

Reviewer #4

(Remarks to the Author)

I co-reviewed this manuscript with Reviewer #3.

K. Maejima et al demonstrated the rapid water adsorption and desorption behaviors on the porous van der Waals crystals. Those rapid adsorption and desorption behaviors are interesting but the water adsorption mechanism should be discussed in detail. The paper must be revised for publication.

The interaction of VPC-1 with water molecules is not clearly mentioned in the manuscript. The authors stated the conformational change of the G2DBPHZ relates to the quick adsorption/desorption behavior of water. In line 144, the author mentioned "We presumed that such a pore is less affinitive to H2O and can accelerate the transportation of H2O in the pores. The conformational change of G2DBPHZ associated with the H2O sorption is also beneficial for enhancing the sorption kinetics because the structural transition often makes the sorption profile discontinuous in analogy to phase transition.". However, how and where the water molecules adsorbed in VPC-1. The author mentioned "Cz dendrons were exposed to the pores." in line 78-79 but it is hard to understand how does this hydrophobic surface strongly interact with water molecules and provide rapid adsorption/desorption of water? Does the pure Cz dendrons also exhibit the rapid water capture/release properties? I could not understand throughout the manuscript, why is VPC-1 the fastest among the reported porous materials as you mentioned in line 86. The adsorption mechanism should be different from the conventional porous materials. Authors must discuss the water adsorption mechanism of VPC-1 along with the porosity of this materials using N2 adsorption analysis.

Followings are minor comments.
p2 line 30: Did you mistake "sutained" for "sustained"?

p6 line 117: I'm curious about the structural stability of the VPC-1 against water. The XRD patterns of the VPC-1 before (0%RH) and after dehumidification should be shown. It would be even better if authors show the XRD pattern after the several repeated tests.

p8 line 148-150: Total water adsorbed amount on VPC-1, activated carbon and silica gel should be shown.

p9 line 171-172: Does irradiation of the laser induce structural change of VPC-1. Or is the structural changes induced by increase of temperature of the powder and/or water molecules? It is not clear whether the temperature increase of water molecule induces the desorption of water or structural changes of VPC-1 induces the desorption.

p10 line 182-183: From which figure can we know the threshold energy is 2.1 mJ cm-1? Explain the meaning of the threshold energy (Eth) clearly.
p10 line 186-188: Water molecules also absorb IR. Is this IR spectrum in Fig.2c measured under vacuum or at a specific humidity? And how large is the temperature increase of the sample upon the samples? The meaning of the sentence ",which proceeded more efficiently when exciting intense IR absorption band of G2DBPHZ" cannot be understood. Proceed what? If authors intended "the photothermal heating is proceeded more efficiently", please correct the sentence into ",which is proceeded more efficiently when exciting intense IR absorption band of G2DBPHZ".

p11 Figure 3d: The left vertical axis label should be written as "Pth (mW cm-2)" and the right as "Tth (mW cm-2)". Author should explain briefly what are Pth and Tth in the figure caption.

p11 line 186-188: Explain the threshold power (Pth) clearly.

p12 line 213-215: Why the authors consider only the temperature effect of visible light and why did not show the temperature increase by IR?

p12 line 224-229: Why do authors choose a method using a cellophane film for detection of the quick release of water? For quantitative analysis, quartz crystal microbalance method or other methods can be applicable. The attempt using this material for a humidifier looks good and it is no doubt the VPC-1 shows the rapid adsorption and desorption behavior and this system can be applicable to an actuator. However, quantitative results containing the amount of water adsorbed/desorbed and time should be provided to justify the superiority of this material than the other materials (activated carbon and silica gel).

p15 line 251-253: Could you also show the time-course change in the height of the film edge (similar to Fig.4c) of activated carbon? The slow adsorption/desorption behavior should provide a slow move of the film. Then, authors can discuss which material is suitable for a humidifier and an actuator.

p15 line 256-258: Why does the desorption of water molecules from the activated carbon decrease by repeating? Did the structure of the activated carbon change by right irradiation? Sample information of activated carbon and silica gel has to be described in the experimental section.

p16 line 276: Correct "humification" into "humidification".

p25 line 510-512: Pre-treatment condition before adsorption measurement should be mentioned.

p33 line 633 (figure caption of Fig. S11): make space between 22.6 and °C.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I have re-reviewed the manuscript in light of my original comments as well as the comments by the other reviewers. All the reviewer comments seem to have been well addressed and I want to commend the authors for this. It's nice to see this level of effort to clarify the work. I am still not convinced that this journal is the right fit for this paper. That being said, if the other reviewers are convinced that this is the right fit, then I am happy to concede and I hope that the reviewer comments help point the authors into some interesting future work that I look forward to reading.

Reviewer #2

(Remarks to the Author)
The authors have adequately addressed my comments for which I thank them.

Reviewer #3

(Remarks to the Author)
The authors have revised the manuscript to my satisfaction. I recommend publication in Communications chemistry.

I have only one comment on the part below.
Are the values for AC and silica gel in the revised manuscript the opposite?
The author should check the water adsorbed amount on AC and silica gel in the revised manuscript.

p8 line 148-150: Total water adsorbed amount on VPC-1, activated carbon and silica gel should be shown.
=> Thank you for your comment. We measured the sorption and found that the total water uptakes of VPC-1, activated carbon, and silica gel are 106.4, 473.7, and 481.1 mL(STP) g–1, respectively.
=> These data are written in the revised manuscript as follows:
“In comparison to the maximum H2O uptake of VPC-1 (6.3 wt%, 106.4 mL(STP) g–1), both silica gel and activated carbon are known to feature larger H2O uptake (20–65 and 16–40 wt%) according to literature27,28,29,30,31,32, which we confirmed by ourselves using the pore & surface analyzer. The experimental values for silica gel and activated carbon used for the actuation experiments were 473.7, and 481.1 mL(STP) g–1.”
(main text, page 19, line 2)

Reviewer #4

(Remarks to the Author)
The authors revised the manuscript quite nicely considering my comments.
I am pleased to recommend the acceptance of this revised version.

Point-to-Point Responses to the Reviewers' Comments

For Reviewer #1:

I have reviewed the manuscript entitled "Molecular crystal with permanent and transformative porosity sustained thoroughly by van der Waals interactions for ultrafast water release" by Yamagishi and coworkers. The work describes the formation of a porous material that is assembled via van der Waals interactions. The porous material is able to adsorb water into the pores and be released by irradiation. Even under sealed conditions, the porous material is able to exert a considerable amount of force by releasing the pressure of the adsorbed water.

I think the manuscript is very well written and the work is convincing. I don't believe further experiments are necessary and the conclusions are supported by the data.

=> Thank you for your appreciation of our achievements.

My primary comments are in the introduction and are likely more stylistic than scientific.

Despite this, I'm not sure that this manuscript is a good fit for Communications Chemistry. As the authors clearly point out, this material has already been shown "slight spectral changes as a function of humidity". As such, I feel that this work is a good follow up but perhaps doesn't fit into the category of "Publishing significant advances across all areas of chemistry". I don't know that this work would influence the thinking in the field (especially given that the material is already known and would have made its impact from the previous publication).

=> The material and its chromism were reported previously as you pointed out, but we still believe that our finding herein is seminal and worth publishing because the focus of the manuscript is not the chromism. The major contents of the submitted manuscripts are as listed below.

Point 1. We newly disclosed single-crystal structure of **VPC-1**.

Point 2. We newly revealed the sorption kinetics of **VPC-1,** which is far faster than conventional porous materials.

Point 3. We newly found that the humidification with **VPC-1** can actuate a film.

=> As for point 1, we newly revealed the single-crystal structures of **VPC-1**. The crystal structures provide the atomic-scale information about how the Cz dendrons move in response to the adsorption of H_2O. The information is valuable because no other porous crystals sustained by van der Waals forces behave like that, which we think is of fundamental significance and is worth publishing in *Commun. Chem*. To make the novelty clearer to the readers, we newly add sentences to the revised manuscript as follows:

"The single-crystal structure revealed herein provide an insight into how the molecules can move within a porous crystal that is sustained by van der Waals interactions."

(main text, page 21, line 8)

=> As for point 2, the sorption kinetics of **VPC-1** (490 μs) is far faster than the conventional porous materials (>7 s). The fast sorption kinetics is not a mere follow-up of the previous report but is, in our opinion, a significant finding that should be appreciated separately from the previous report.

=> As for point 3, we find that the desorbed H_2O vapor is intense and induce bending of a film. This finding is totally distinct from the contents reported in the previous paper.

=> Altogether, the contents in the present paper are distinct from our previous study and is not a report that "made its impact from the previous publication". We think that there is no consensus within the scientific community that the novelty of a paper is invalidated solely because the material used and its supplemental property have been previously reported.

Page 4 the authors mention "Reticular bonding network together with flexible linkers and deformable bonds". As a porous materials person, I'm not sure I could define reticular bonding.

=> Thank you for your comment on the terminology. We used the phrase "reticular bonding" to indicate the network of strong intermolecular interactions. More specifically, we indicated the networks of coordination bonds, hydrogen bonds, and dynamic covalent bonds that have been introduced for the synthesis of metal–organic frameworks (MOFs), covalent-organic framework (COFs), and hydrogen-bonded frameworks (HOFs). We quoted the word "reticular" from the authentic papers reported by other researchers including, for instance, Prof. Yaghi's and Prof. Farha's groups (*Nature* **2003**, *423*, 705; *Acc. Chem. Res.* **2022**, *55*, 579). Nonetheless, following your suggestion, we replace the words with "intermolecular bonding network" or and "bonding network" for better readability in the revised manuscript.

In addition, to make the meaning of "bonding network" clearer to the readers, we insert a sentence in the revised manuscript as follows:

"The intermolecular bonding network with sufficient bonding strength makes the porous framework robust and tolerant against the evacuation of the guest molecules"

(main text, page 3, line 5)

the authors state that "porous van der Waals crystals ... have been beyond the scope of crystal engineering because the conventional reticular bonding strategy is unapplicable". Again, it's not clear to me what reticular bonding is, and it's not clear to me that van der Waals materials could have them.

=> Thank you for your comment. The definition of the reticular bonding is written above. As seen in MOFs, COFs, and HOFs, these porous crystals have been synthesized by connecting the constituent organic molecules via strong intermolecular bonds such as coordination, dynamic covalent, and hydrogen bonds. Obviously, such molecular design is inapplicable to van der Waals crystals in definition since they are no longer a van der Waals crystals if they are harnessed with those bonding motifs.

=> To make this point clearer to the readers, we revise the manuscript as follows:

"Porous van der Waals crystals are one of the most fragile classes of porous materials sustained thoroughly by van der Waals contacts and have been beyond the scope of crystal engineering because the conventional bonding network strategy based on strong intermolecular interactions is unapplicable.”

(main text, page 3, line 5)

Furthermore, I'm not sure that it's true that something is beyond the scope of crystal engineering. I think we haven't come up with design principles for it yet, and I'm not sure this work introduces those critical design elements for others to work from. I just know that this molecule works.

=> Thank you for your comment on the statement of general difficulty of the field. We would like to first revisit the current status of the field. As thoroughly introduced in the authentic reviews from Prof. Cooper and Prof. McKeown together with mine (references 2, 3, and 5 in the original manuscript), porous crystals sustained thoroughly by van der Waals interactions are extremely rare (less than 20) in comparison to the vast families of MOFs, COFs, and HOFs. This is because the molecular packing of van der Waals crystals are unpredictable even with the latest computational technology. In addition, no empirical molecular design strategy has been introduced so far. Actually, molecules forming porous van der Waals crystals are totally different with each other, and even a slight substitution of the molecular structure resulted in the collapse of the pores, a representative case of which was introduced in the review from Prof. Allcock (references 12 in the original manuscript).

=> We would like to also emphasize that the novelty stated in the manuscript is not the establishment of the molecular design for the synthesis of porous van der Waals crystals but the finding of porous van der Waals crystals with flexible and permanent porosity (original version of the manuscript, page 4, line 72). We think the finding and its novelty are worth publishing as written in the answers above.

=> To make the novelty clearer to the readers, we newly added sentences as follows:

“Incorporating flexibility into van der Waals porous crystals, namely, synthesis of van der Waals crystals with flexible and permanent pores are an even more formidable challenge and has never been achieved so far.”

(main text, page 4, line 1)

Similar to point b, "hardly designable" seems a bit harsh given that I'm not sure that this molecule was designed (or at least it's not clear to me from this manuscript that this molecule was designed for this outcome).

=> Thank you for your comment. We meant to express the general difficulty in designing porous van der Waals crystals rather than expressing that we have overcome that.

=> To make the meaning more understandable to the readers, we revised the sentences as follows:

“Such a delicate and intricate molecular packing is hardly designable in general even with the latest crystal engineering technique”

(main text, page 3, line 21)

"to our knowledge" should be removed. Every word we write is "to our knowledge".

=> Thank you for your comment on the expression. Following your instruction, we remove the phrase from the revised manuscript.

I think it's interesting that this is a polar spacegroup.

=> Thank you for your insightful comment on the crystal structure. As pointed out by the referee, *Cm* is a polar space group, while we are not sure how influential it is to the sorption and chromic properties of **VPC-1**. Thus, we revise the manuscript just to indicate that it is a polar space group as follows:

=> "The crystal belonged to the polar space group of *Cm*"

(main text, page 6, line 6)

the authors state "for porous crystals since the kinetics dominates the separation efficiency". It's not clear to me why this would be true. Given large enough pores, thermodynamics would dominate separation efficiency. I don't know that there is a lot of data out there to support where kinetic separation stops and thermodynamic separation starts (with regards to pore aperture size or other functional components of the pores).

=> Thank you for your insightful comment on the separation with porous materials. As you pointed out, the thermodynamic sorption property of the pores as well as the kinetics is influential to the separation efficiency. More specifically, the overall separation efficiency is given by the product of the diffusivity selectivity and sorption selectivity according to a review (*Chem. Rev.* **2020**, *120*, 8161).

=> To include this information, we revise the sentences as follows:

"Sorption kinetics is one of the key figures of merit for porous crystals since the diffusivity as well as sorption selectivity dominates the separation efficiency[23] and charging/discharging rates of guests."

(main text, page 9, line 16)

I'm not sure that I can reproduce the adsorption data. The experimental is not well defined other than the instrument used (and I admit that I am not familiar with that instrument) but kinetic data is not often something that a static adsorption instrument can produce. Also, any adsorption data should be reported in an AIF file for others to be able to examine (similar to any CIF file).

=> Thank you for your comments on the experimental methods. We revised the method sections to include the experimental procedures of the adsorption measurements as follows:

"**VPC-1** was degassed at 50 °C for at least 24 h prior to the measurements. The adsorption rates were evaluated at 25 °C by monitoring the time-dependent change in pressure after the introduction of a fixed volume of H_2O vapor into the sample chamber, using the BELSORP MAX application."

(Supplementary Information, page 29, line 6)

=> The AIF files of the adsorption isotherms were newly uploaded as supporting data.

For Reviewer #2:

Yamagishi and co-workers present a high quality investigation in which they illustrate a van der Waals crystal applied to ultrafast water release.

As the computational reviewer, I will defer comments on the synthesis and characterization to my reviewer colleagues and focus on the computation. The computation in this manuscript consists of simulation of the IR spectrum as they key dihedrals change. This is completed using an appropriate computational method and I have no problems with the calculations that were done.

=> Thank you for your high appreciation of our achievements.

I do think, that the authors, particularly with their stated aims of designability, could do a lot more with their calculations, that would lend a lot of support both to the arguments in this manuscript and the future work of these authors and others.

Simple calculations that would increase the impact of the manuscript:

=> We thank the referee for his/her suggestion. We have calculated the interaction energy for π-π dimers extracted from crystal X-ray data and reoptimized at the ωB97XD/6-31G** level (see Figure S8, included in the revised Supporting Information). We have found that pi-pi stacking for dimers extracted from the crystalline structures is much higher in the crystal under vacuum (~-113 kcal/mol) when compared to those hydrated (~-60 kcal/mol). This might be due to the more planar DBPHZ cores observed under vacuum that results in much higher pi-pi stacking energy. On the other hand, similar pi-pi stacking energies and structural conformation are obtained for the three optimized dimers regardless of the starting crystal structure. This can be ascribed to the facility of the outer arms of the carbazole to rotate and accommodate in such a way as to maximize π-π interactions.

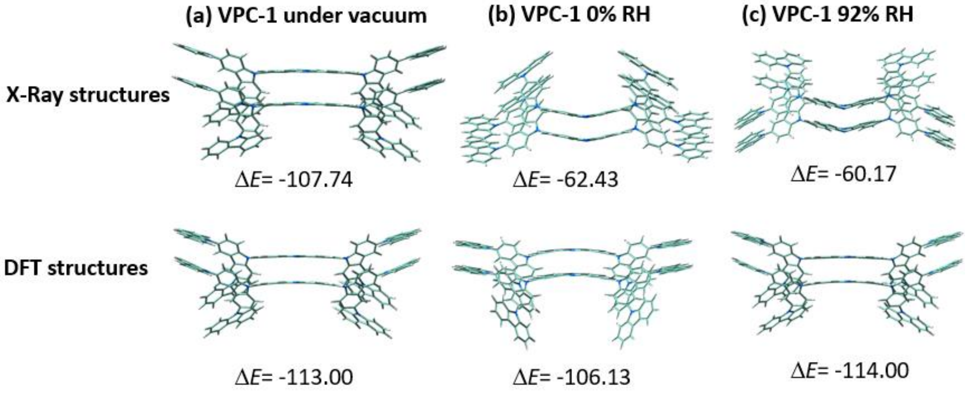


Figure S8. Interaction energies, Δ*E* (kcal mol^{-1}), for π-π dimers extracted from crystal X-ray data (upper part) and reoptimized at the ωB97XD/6-31G** level of theory (lower part) for **VPC-1** under vacuum (a), under 0 %RH (b) and under 92 %RH (c).

Inter-column interactions (i.e. interactions between molecules in the ab and ac directions) - either a dimer calculation using DFT and/or a semi-empirical calculation (DFTB) of a whole column.

=> As suggested by the reviewer, we have computed the interaction energies for dimers extracted from the crystal structures along the different directions. We found that the interactions between molecules in the ab and ac directions are an order of magnitude smaller compared to the interactions along the pi-pi stacking. This is observed for both vacuum (Figure S3) and hydrated crystalline structures (Figure S10 and S11), showing that the intercolumnar interactions in these structures are very weak compared to pi-pi interactions.

To include this information, we incorporate this new sentence in the revised manuscript:

"DFT-calculations for dimers extracted from the crystal structures along the different directions support that the intercolumnar interaction are very weak compared to pi-pi interactions (Figure S4)"

(main text, page 6, line 19)

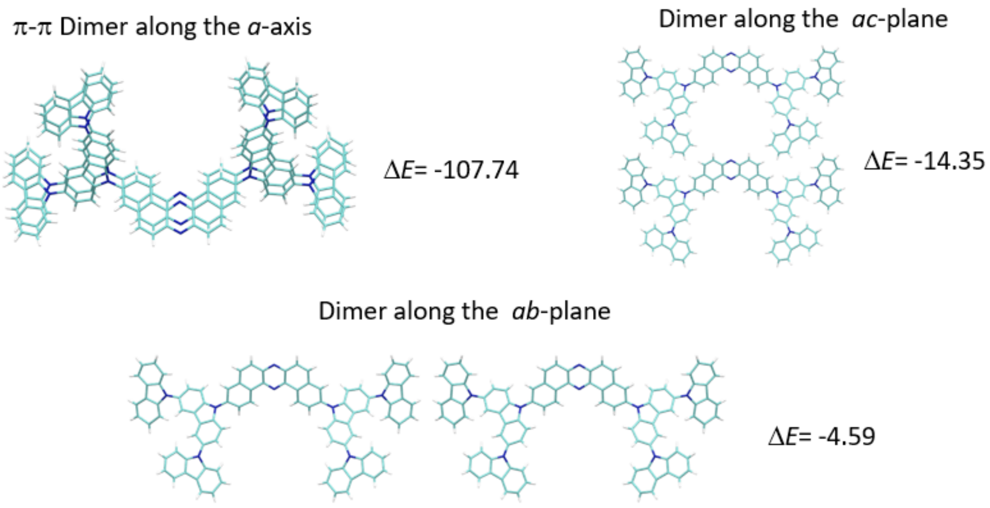
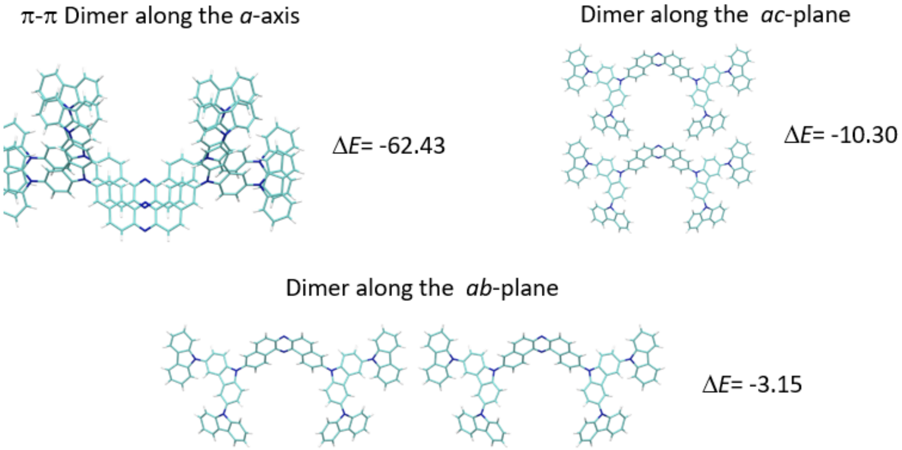


Figure S3. Interaction energies, Δ*E* (kcal mol^{-1}), for dimers along various crystal directions extracted from the crystal packing of **VPC-1** under vacuum, calculated at the ωB97XD/6-31G** level of theory.


π-π Dimer along the *a*-axis

ΔE= -62.43

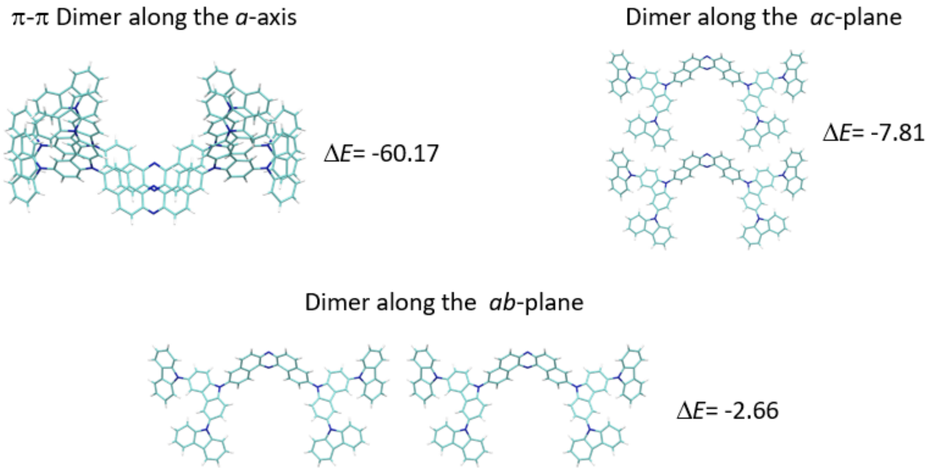
Dimer along the *ac*-plane

ΔE= -10.30

Dimer along the *ab*-plane

ΔE= -3.15

Figure S10. Interaction energies, ΔE (kcal mol^{-1}), for dimers along various crystal directions extracted from the crystal packing of **VPC-1** under 0 %RH, calculated at the ωB97XD/6-31G** level of theory.


π-π Dimer along the *a*-axis

ΔE= -60.17

Dimer along the *ac*-plane

ΔE= -7.81

Dimer along the *ab*-plane

ΔE= -2.66

Figure S11. Interaction energies, ΔE (kcal mol^{-1}), for dimers along various crystal directions extracted from the crystal packing of **VPC-1** under 92 %RH, calculated at the ωB97XD/6-31G** level of theory.

Interaction energy of water in each identified binding site.

=> Following the reviewer's suggestion, we have performed the optimization of a pi-pi stack dimer by including one or two H_2O molecules. These calculations confirm that the H_2O molecules form hydrogen bonds between them and also with the nitrogen of the central DBPHZ core (that is, smaller than the sum of Van der Waals radii). On the other hand, calculations reveal that the interaction energy of water at each identified binding site is of the order of 25 kcal/mol, i.e. about six times smaller than the pi-pi energies.

To include this information, we incorporate this new sentence in the revised manuscript:

"DFT-optimized geometries of a **G2DBPHZ** dimer with one and two H_2O molecules support the formation of hydrogen bonds between the H_2O molecules and with the N atoms of the DBPHZ core (Figure S13). The binding energies of the H_2O molecules is doubled by the presence of the second H_2O molecule; however, our results shows that π−π stacking interactions has higher contribution to aggregation than the hydrogen bonding to water (*i.e.*, compare Figure S13 with Figure S8).

(main text, page 8, line 21)

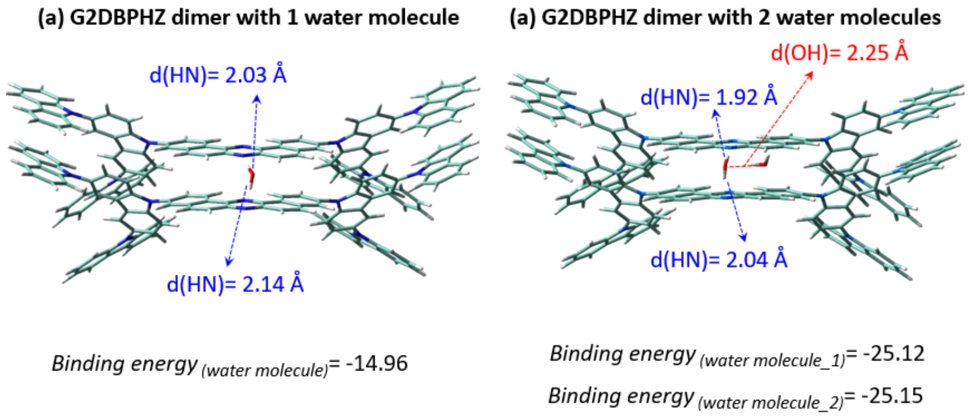


Figure S13. DFT-optimized geometries of a **G2DBPHZ** dimer with a H_2O molecule (a) and two H_2O molecules (b), calculated at the ωB97XD/6-31G** level of theory. The binding energies of the H_2O molecules (in kcal mol-1) and the hydrogen bond distances formed between the H_2O molecules and with the N atoms of the DBPHZ core.

Potential energy surface (i.e. scan) of the highlighted dihedral angles - and then link this back to the pi-pi stacking energy above

=> As suggested by the reviewer, the potential energy surface for the rotation around the central skeleton of DBPHZ and adjacent carbazole has been explored by DFT calculations. A rather flat torsional potential has been found. This explains the ease of the outer arms of the carbazole to rotate and accommodate in such a way as to maximize pi-pi interactions. In fact, the vacuum crystal has a rotation of this dihedral of about 47 degrees, while upon wetting it rotates up to 70 degrees, as a consequence of the ease of rotation of these side groups.

To include this information, we incorporate this new sentence in the revised manuscript:

"The conformational flexibility of the Cz dendrons with respect to the central DBPHZ core has been explored computationally. Interestingly, a rather flat torsional potential has been found, with a small energy difference of 3.3 kcal/mol between the perpendicular conformation and the most stable conformer with a dihedral angle of ~ 50º (Figure S7). This explains the facility of the outer arms of the carbazole to rotate and accommodate in such a way as to maximize π-π interactions, adjusting the transformation of the crystal structure after adsorption (Figure S8-S11)."

(main text, page 8, line 3)

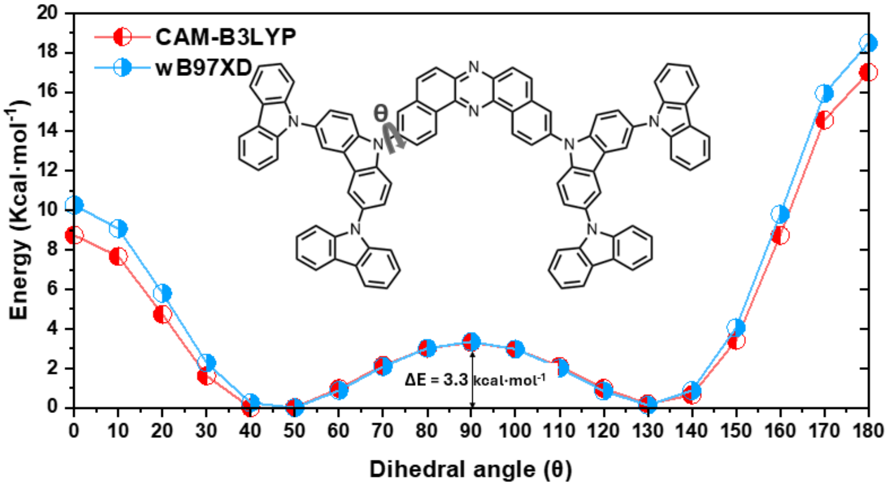


Figure S7. Rigid potential energy surface scan of **G2DBPHZ** as a function of the inter-ring dihedral angle (θ) between central DBPHZ spacer and the adjacent carbazole unit, calculated at the CAM-B3LYP/6-31G** and ωB97XD/6-31G** level of theory, respectively.

A defect calculation (i.e. take the crystal structure and do a single point calculation after subtracting one molecule: deltaE(defect) = E(crystal) - [E(crystal - molecule) + E(molecule)]

=> Following the reviewer´s suggestion, we have computed defect calculations for a stack of 7 molecules after subtracting one molecule. As seen in Figure S9, very large defect energy values are found when a molecule is extracted from a pi-pi stacked column with larger values found for the crystal under vacuum (–228.05 kcal/mol) when compared to those hydrated (~ –136 kcal/mol). These results confirm again the strong crystalline packing along the columns, in line with the large pi-pi stacking energies previously calculated for dimers as displayed in Figure S8 (see the reply to the first comment of reviewer 1).

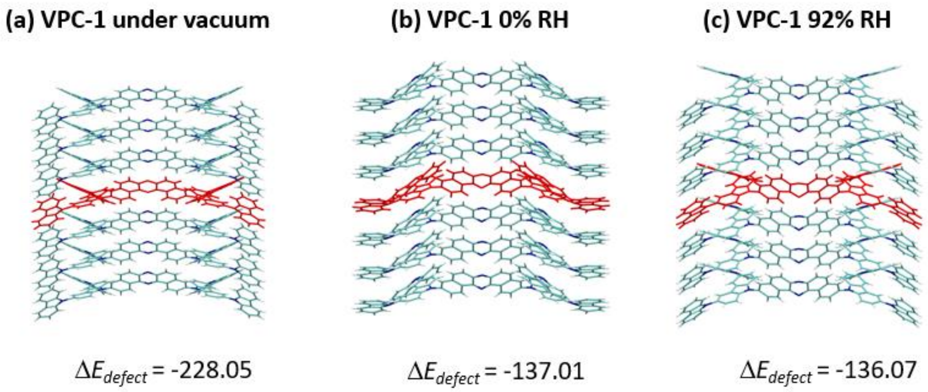


Figure S9. Interaction energies, ΔEdefect (kcal mol^{-1}), for seven π-π stacked molecules extracted from the crystal packing of **VPC-1** under vacuum (a), under 0 %RH (b) and under 92 %RH (c). The defect energies has been evaluated as follows: ΔEdefect = E(7 stacked molecules) - [E(7 stacked molecules – central molecule) + E(central molecule)].

Line 244: For ease of navigation, please mention the section of the SI where the details can be found.

=> Thank you for your comment. We have added the name of the corresponding section as follows:

"(see Actuation experiments of cellophane films with **VPC-1** section in Supporting Information for the details of the calculation)"

(main text, page 17, line 5)

For Reviewer #3:

K. Maejima et al report the water adsorption behavior on porous organic crystals. The observed adsorption behavior sounds interesting. However, the adsorption behavior is not necessarily well understood, even though authors assisted the fast water adsorption on their molecular crystals. The paper must be revised for publication.

=> Thank you for your appreciation of our achievements and comments on the revisions.

Water adsorption on the sample crystals is the most key in the paper. The most important point is not necessarily quantitatively described. The water adsorption isotherm must be measured after the optimum preheating. The pore volumes assessable to N2 at 77 K and water at 298 K (room temp) can give the quantitative discussion. As water easily condenses on the sites at lower temperature in the adsorption system, quite accurate temperature control is requested. Then, authors can discuss how much pore spaces are occupied by N2 at 77 K and water at 298 K, giving the fractional filling using the pore volume derived from XRD and the observed adsorption amounts using the liquid density of N2 and water at adsorption temperature.

=> Thank you for your insightful comments on the adsorption measurements. We omitted the H_2O adsorption data in the original manuscript because they were reported in our previous paper and was cited as reference 22 in the original manuscript. As a response to your request, we reproduced the N_2 and adsorption isotherms of **VPC-1** at 77 K and its H_2O versions measured at 283, 293, and 303 K in the revised manuscript as Figure S12. Together with the figure, we add explanations about the results as follows:

"The N_2 and H_2O adsorption isotherms of **VPC-1** were reported previously and were reproduced in the supplementary information as Figure S12. The abrupt increase in N_2 uptake at lower P/P_0 region indicates the micro-porosity of **VPC-1**, which is consistent with the single crystal structure shown in Figure 1a. The adsorption of H_2O in **VPC-1** happens abruptly at $P/P_0 = 0.5$, although the cause of the abrupt increase was not evident in the previous paper. Judging from the crystal structures revealed herein, we presume that the sudden uptake of H_2O and the structural change of **VPC-1** happens simultaneously. The transformation of the porous framework may allow the H_2O molecules to form clusters with optimum geometry and thereby suddenly accelerate the uptake of H_2O. The hydrogen bonds between guest H_2O molecules and the nitrogen atoms of DBPHZ that are exposed to the pore may be also influential to the structural transition, while it is not conclusive due to the uncertainty of the location of H_2O.

The pore volume of **VPC-1** calculated based on the single-crystal structure was 737 Å^3 per unit cell ($V = 3646.39$ Å^3) for N_2 and 780 Å^3 for H_2O. The fractional filling for N_2 at $P/P_0 = 0.96$ and 77 K is 26%, and the fractional filling for H_2O at $P/P_0 = 0.92$ at 293 K is 36%. The relatively low pore filling is attributed to the one-dimensional pores of **VPC-1**, which is often stuck and becomes inaccessible with the gas."

(main text, page 8, line 10)

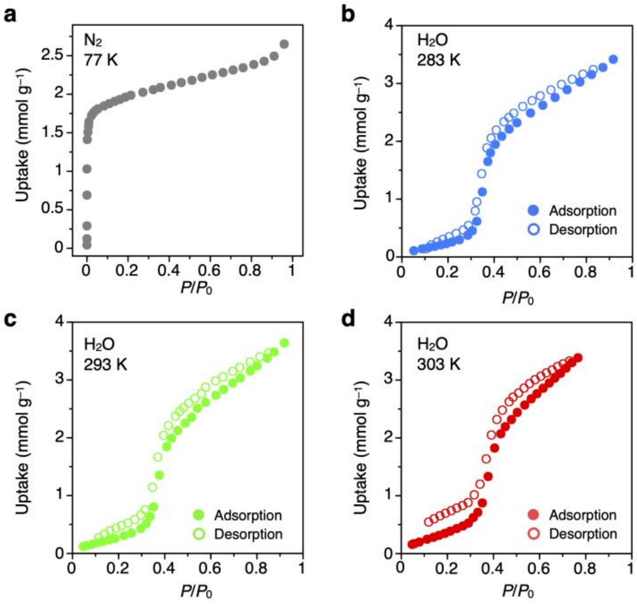


Figure S12. N_2 (a) and H_2O (b–d) isotherms of **VPC-1** measured at 77, 283,293, and

303 K, respectively.[22]

=> Judging from the values, the accessible pores are relatively little in **VPC-1**, which is often observed with microporous materials with one-dimensional pores.

=> The adsorption and desorption curves in Figure S12 are smooth and show no significant hysteresis at every temperature examined. These results indicate that the condensation of water on **VPC-1** is negligible in the measurements and prove the accuracy of the temperature control of our measurements.

120 page 6: The samples are not sufficiently pre-treated. Authors may clarify the residual water in the crystals. The optimum preheating conditions must be determined. The strong adsorption sites such as crystal defects and chemical sites may be shown. The irreversibility must be qualitatively described.

=> Thank you for your comment on the pre-treatment and the reversibility of sorption. The detailed experimental procedures of the pre-heating were written in the revised manuscript as follows:

"**VPC-1** was degassed at 50°C for at least 24 h prior to the measurements. The adsorption rates were evaluated at 25 °C by monitoring the time-dependent change in pressure after the introduction of a fixed volume of H_2O vapor into the sample chamber, using the BELSORP MAX application."

(supplementary information, page 29, line 6)

=> The H_2O sorption of **VPC-1** is reversible without any detectable H_2O remained in the pores. The H_2O isotherm measurements in Figure S12 b–d, were conducted continuously with the same specimen by conducting the same pre-treatment for every measurement. The isotherms show virtually identical profiles with each other at lower P/P_0, meaning that H_2O adsorbed in the pores are removed almost completely during the pretreatment and that the H_2O sorption characteristics of **VPC-1** remained intact even upon repeating the H_2O adsorption and desorption. Sentences including this discussion are newly added to the revised manuscript as follows:

"The isotherms of Figure S12b–d were conducted with the same specimens, indicating the intactness of the H_2O adsorption performance of **VPC-1** even upon repeating the H_2O adsorption and desorption."

(main text, page 9, line 10)

144 page 8: Could you show the reason why authors use "less affinitive to H2O " instead of hydrophobic ? Why the less-affinitive pores accelerate the transportation of water inside the pores?

=> Thank you for your comment. We used the word "less affinitive" because the pore is not completely hydrophobic but is slightly affinitive to H_2O due to the nitrogen atoms in carbazole and DBPHZ and can uptake certain amount of H_2O molecules (Figure 1b).

=> As is found in a review (*Chem. Soc. Rev.* **2012**, *41*, 3099), the adsorption energy is inversely correlated to the diffusivity of the guests in general. This is because the stronger adhesion to the pore surface inhibits the detachment of the guest molecules and following transportation in the pore.

=> To make this point clearer to the readers, we revise the manuscript as follows:

"Considering the general understanding that weaker adhesion to the pore surface accelerate the diffusion of the guest molecules in the pores,[24] we presumed that the pores in **VPC-1** is less affinitive to H_2O and can accelerate the transportation of H_2O in the pores."

(main text, page 9, line 22)

Authors mention that their crystals can adsorb very rapidly H2O. However, this is not clearly shown, as given in 4.

148-150 page 8: Authors assist that their crystals can quickly adsorb water compared with other porous materials. This comparative discussion is quite insufficient.

For example, authors mention the adsorption time on their crystals is about a half of that on activated carbon. There are so many kinds of activated carbons. If authors use high surface area activated carbons having many surface functional groups should show much shorter time. Then, "faster" is not evident. The more rigorous comparison should be necessary.

Also, zeolites show attractive water adsorption behavior and then the adsorption rate of several zeolites may be measured for the comparison, too.

=> To address the requests from the referee, we newly measured H_2O adsorption kinetics of activated carbon specialized for neutral gaseous molecules (UES Co., Ltd., USG-CT-S-200), zeolite (zeolite A-5), and multi-walled carbon nanotubes (TCI, C2155) as a totally hydrophobic porous carbon (Figure S15). The profile of **VPC-1** is clearly distinct from the others in that the curve shows a drastic drop just after introducing the H_2O vapor. The half decay periods of the H_2O pressure observed for **VPC-1**, carbon nanotubes, activated carbon specialized for neutral gaseous molecules, and zeolite are 1.5, 7.7, 21.0, and 14.0 sec. The activated carbon listed in the original manuscript (UES Co., Ltd., USG-PT-SX-200) was designed for capturing common gasses according to the product specifications and showed half decay periods of 9.6 sec. Except **VPC-1**, carbon nanotubes showed the fastest sorption kinetics, which is consistent with our claim that the hydrophobic pore accelerates the H_2O sorption. Please also note that the actual time constant for **VPC-1** based on the optical measurement is 490 μs, which is too fast to be measured with the specific surface area & pore size analyzer.

=> We revise the manuscript to include these new data as follows:

"**VPC-1** showed a drastic drop in the pressure just after introducing the H_2O vapor, which is distinct from those of conventional porous materials including two types of activated carbons, carbon nanotubes, and zeolite (Figure S15). The half decay period of the H_2O pressure observed for **VPC-1**, two types of activated carbons, carbon nanotubes, and zeolite were 1.5, 9.6, 21.0, 7.7 and 14.0 sec. The faster H_2O sorption kinetics of **VPC-1** was appreciable"

(main text, page 10, line 7)

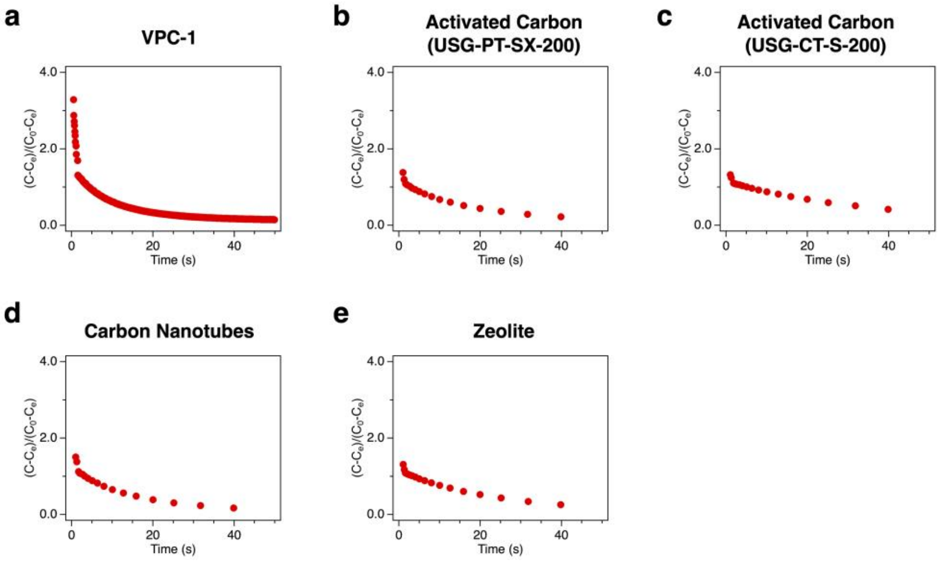


Figure S15. Time-course profile of $(C–C_e)$ / $(C_0 – C_e)$ at 25 °C when introducing H_2O vapor to **VPC-1** (a), activated carbon for common gas (UES Co., Ltd., USG-PT-SX-200) (b), activated carbon for neutral gas (UES Co., Ltd., USG-CT-S-200) (c), carbon nanotubes (d), and zeolite A-5 (e). C is the concentration of water vapor, C_0 is the concentration of water vapor at t = 0 s, and C_e is the concentration of water vapor at equilibrium.

156 page 8: Can you remove the residual water by IR laser irradiation?

=> Thank you for your question. We do not think that the residual water can be removed totally by the irradiation of IR. As shown in Figure S18, the change in diffuse reflectance of **VPC-1** increases even at E larger than 100 mJ cm^{-2}, indicating that H_2O in **VPC-1** is released continuously. In addition, it is technically unachievable for us to quantify the residual amount of H_2O in **VPC-1** during the IR excitation since, as written above, the setup for IR irradiation cannot be integrated with the sorption machine. In addition, the desorption of H_2O upon irradiation of IR is temporal and is difficult to monitor with conventional methods.

156-157 page 8: Did you examine the possibility of the crystal degradation during the IR laser irradiation? Can you describe the temperature change on the irradiation?

=> Thank you for your question. We do not think the degradation of **VPC-1** during the IR irradiation is significant. The plots in Figure S18 were measured with the same specimen but show no chronological changes.

=> We cannot measure the temperature of **VPC-1** during the irradiation of IR pulses due to the limitation of setup and the fast rise and fall time of temperature change (<0.5 s). We would like to also tell that the installation of thermometer to probe the sample temperature is technically difficult. The source and facility for generating visible light and IR pulses are totally different. The visible light is generated from a portable light source with a dimension of approximately 40 x 50 x 30 cm, and the light can be guided using an optical bundle fiber. On the other hand, the IR pulses are generated from free electron laser that occupies a whole house with a dimension of roughly 10 x 10 x 10 m. The experimental setup is mostly prefixed by the manager of the facility, and we do have so much freedom in customizing the sample chamber. We designed a sample chamber that can be installed in that facility. To visualize the configuration of the sample chamber, we newly added a detailed schematic illustration as Figure S16 to the revised manuscript. As shown therein, the sample space is thin, and the chamber is totally sealed except the inlet and outlet for the vapor. Therefore, it is difficult to embed the sensor tip into the power of **VPC-1** in the steel chamber.

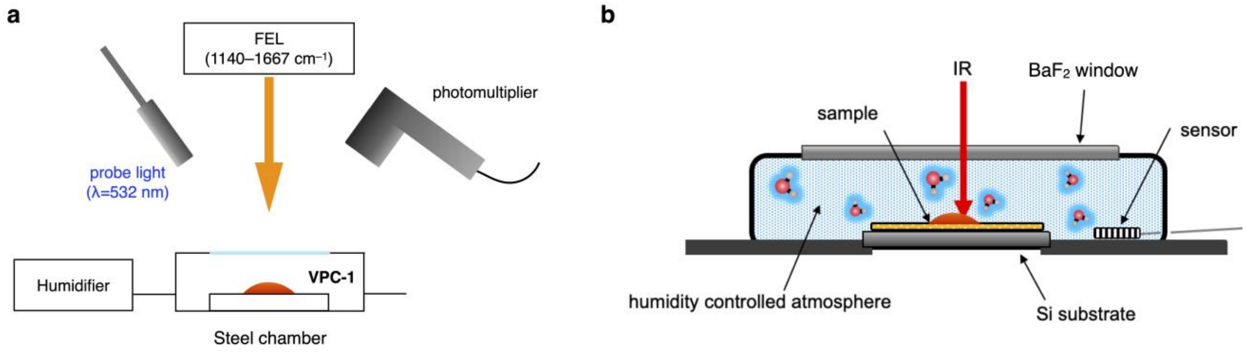


Figure S16. (a) Schematic illustration of the experimental setup for measuring diffuse reflectance of **VPC-1**, which was pumped with the infrared light generated from the free electron laser. (b) Detailed schematic illustration of the chamber.

=> Nonetheless, we can assume the temperature of **VPC-1** during IR irradiation judging from the threshold power. At threshold, the temperature of **VPC-1** should be 26 °C according to Figure 3d. The temperature at *E* higher that threshold is higher than that although its quantitative measurements is unachievable.

=> We revise the manuscript to include this interpretation as follows:

"The IR pulses at E_{th} are also supposed to increase the temperature of **VPC-1** to 26°C."

(main text, page 15, line 13)

162 page 8: Water vapor condenses easily on the sites having a lower temperature. Authors may show the uniformity of the temperature on measuring. The temperature must be controlled within ±0.05 K at least.6.

=> The temperature of the steel chamber is stabilized within ±0.05 K. Thus, we think the data is trustworthy.

=> We revise the manuscript to include this information as follows:

"The temperature of the chamber is stabilized within ±0.05 K."

(supplementary information, page 28, line 33)

183-185 page 10: Authors can explain the relationship between adsorption and molecular motion more precisely.

=> Thank you for your comment. That is one of the most fundamentally intriguing discussions in this study, but we, in the original submission, decided not to write them because the relationship was not fully conclusive due to the uncertainty of the location of H_2O molecules. The experiment was conducted at room temperature and was analyzed by Rietveld refinement method, resulting in the huge disorder of the location of H_2O molecules. Please note that the severe disorder of guest molecules is typical for crystals observed at room temperature. Nonetheless, as a response to your request, we add a discussion paragraph to the revised manuscript regarding the possible relationship between the adsorption and the structural change as follows:

"The adsorption of H_2O in **VPC-1** happens abruptly at $P/P_0 = 0.5$, although the cause of the abrupt increase was not evident in the previous paper. Judging from the crystal structures revealed herein, we presume that the sudden uptake of H_2O and the structural change of **VPC-1** happens simultaneously. The transformation of the porous framework may allow the H_2O molecules to form clusters with optimum geometry and thereby suddenly accelerate the uptake of H_2O. The hydrogen bonds between guest H_2O molecules and the nitrogen atoms of DBPHZ that are exposed to the pore may be also influential to the structural transition, while it is not conclusive due to the uncertainty of the location of H_2O."

(main text, page 8, line 13)

=> We also add a sentence that indicate the uncertainty of the crystal structure regarding to the location of H_2O as follows:

"', revealing the crystal structures of **VPC-1** including H_2O although the location of H_2O is partially uncertain."

(main text, page 7, line 6)

189 page 10: Could you discuss on the effect of IR-excitation on water adsorption?

=> Thank you for your comment. The discussion on the effect of IR excitation on water *desorption* was written at lines 186–188 in page 10 in the original manuscript. We think that IR pulses heat **VPC-1** and induce the desorption of H_2O. The heated **VPC-1** is cooled by the surrounding atmosphere eventually after the IR pulse irradiation and *adsorbs* H_2O from the atmosphere, which is evident from the gradual recovery of diffuse reflectance as shown in Figure 2a. The recovery of the H_2O adsorption and the diffuse reflectance is nearly perfect.

=> To make the adsorption process clearer to the readers, we revise the manuscript as follows: "The photothermally heated **VPC-1** is then cooled by the surrounding atmosphere eventually after the IR pulse irradiation and adsorbs H_2O from the atmosphere, which is evident from the gradual recovery of diffuse reflectance (Figure 2a)."

(main text, page 12, line 18)

page11: Could you discuss on the effect of visible-light irradiation on water adsorption? Is there any structural change in the pore walls?

=> Thank you for your comment. Similar to the case of IR irradiation, we think the heat generated by photothermal effect induces the desorption of H_2O from **VPC-1**. However, it is difficult to analyze the crystal structure of **VPC-1** in the middle of the light irradiation because we cannot integrate the light sources as well as the sample chamber with humidity and temperature controller into our X-ray diffractometer since it is tightly sealed and enclosed in a protective wall.

For Reviewer #4:

I co-reviewed this manuscript with Reviewer #3. K. Maejima et al demonstrated the rapid water adsorption and desorption behaviors on the porous van der Waals crystals. Those rapid adsorption and desorption behaviors are interesting but the water adsorption mechanism should be discussed in detail. The paper must be revised for publication.

=> Thank you for your appreciation of our achievements and comments on the revisions.

The interaction of VPC-1 with water molecules is not clearly mentioned in the manuscript. The authors stated the conformational change of the G2DBPHZ relates to the quick adsorption/desorption behavior of water. In line 144, the author mentioned "We presumed that such a pore is less affinitive to H2O and can accelerate the transportation of H2O in the pores. The conformational change of G2DBPHZ associated with the H2O sorption is also beneficial for enhancing the sorption kinetics because the structural transition often makes the sorption profile discontinuous in analogy to phase transition.". However, how and where the water molecules adsorbed in VPC-1.

=> Thank you for your question on the location and interaction of H_2O. We decided to write little about the location of the H_2O molecules in **VPC-1** in the original manuscript because of the inaccuracy of the structural analysis. While the location and conformation of DBPHZ was assignable, it was difficult to locate the H_2O molecules precisely. This is because the PXRD profiles were taken at room temperature, inducing severe thermal movements of H_2O molecules. Please note that such sever disorder of guest molecules at room temperature is typical for most of the porous materials.

=> To make this point clear to the readers, we revise the manuscript as follows:

"‚revealing the crystal structures of **VPC-1** including H_2O although the location of H_2O is partially uncertain"

(main text, page 7, line 6)

"The hydrogen bonds between guest H_2O molecules and the nitrogen atoms of DBPHZ that are exposed to the pore may be also influential to the structural transition, while it is not conclusive due to the uncertainty of the location of H_2O."

(main text, page 8, line 19)

The author mentioned “Cz dendrons were exposed to the pores.” in line 78-79 but it is hard to understand how does this hydrophobic surface strongly interact with water molecules and provide rapid adsorption/desorption of water? Does the pure Cz dendrons also exhibit the rapid water capture/release properties? I could not understand throughout the manuscript, why is VPC-1 the fastest among the reported porous materials as you mentioned in line 86. The adsorption mechanism should be different from the conventional porous materials. Authors must discuss the water adsorption mechanism of VPC-1 along with the porosity of this materials using N2 adsorption analysis.

=> Thank you for your questions on the molecular interactions between H_2O and the pore surface as well as its mechanism. We would like to first answer to the question about the adsorption analysis. We wrote little about the sorption isotherms of **VPC-1** in the original manuscript because they were written in our previous paper and was cited as reference 22 in the original manuscript. To display these data to the readers more clearly, we reproduce the isotherm profiles in the revised supplementary information section as Figure S12.

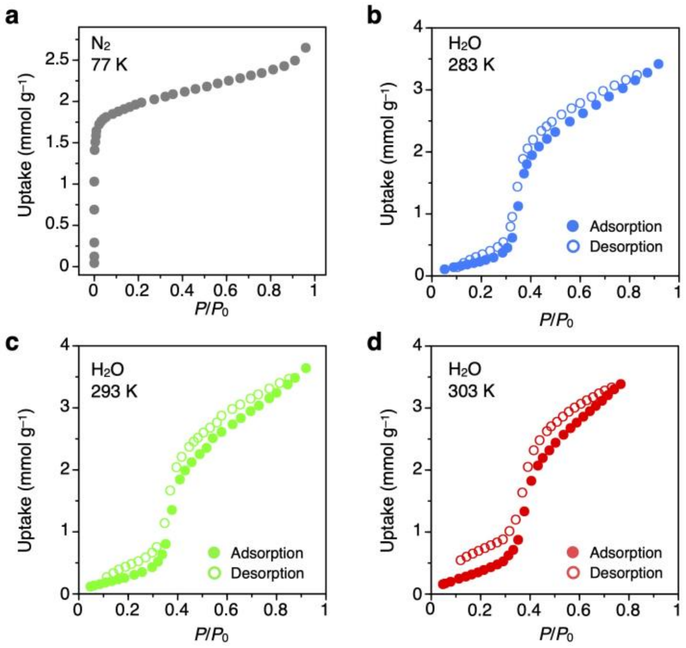


Figure S12. N_2 (a) and H_2O (b–d) isotherms of **VPC-1** measured at 77, 283,293, and 303 K, respectively.[22]

=> We did not write the details about the interactions between Cz and H_2O because of the inaccuracy of the location of H_2O, which is due to the thermal movement of the H_2O molecules. It is a common phenomenon for the crystal structures taken at room temperature. As a response to your request, we add a paragraph explaining plausible interactions between

Cz and H_2O in the revised manuscript as follows:

"The N_2 and H_2O adsorption isotherms of **VPC-1** were reported previously and were reproduced in the supplementary information as Figure S12. The abrupt increase in N_2 uptake at lower P/P_0 region indicates the micro-porosity of **VPC-1**, which is consistent with the single crystal structure shown in Figure 1a. The adsorption of H_2O in **VPC-1** happens abruptly at $P/P_0 = 0.5$, although the cause of the abrupt increase was not evident in the previous paper. Judging from the crystal structures revealed herein, we presume that the sudden uptake of H_2O and the structural change of **VPC-1** happens simultaneously. The transformation of the porous framework may allow the H_2O molecules to form clusters with optimum geometry and thereby suddenly accelerate the uptake of H_2O. The hydrogen bonds between guest H_2O molecules and the nitrogen atoms of DBPHZ that are exposed to the pore may be also influential to the structural transition, while it is not conclusive due to the uncertainty of the location of H_2O."

(main text, page 8, line 10)

=> It is known that weaker adhesion of the guest molecules to the pore surface led to the faster transportation in the pores (*Chem. Soc. Rev.* **2012**, *41*, 3099). Based on this understanding, we presume that the hydrophobicity of Cz may accelerate the transportation of H_2O in the pores, although the H_2O sorption kinetics of pure Cz dendron is hardly predictable because the sorption performance is not solely dependent on the surface chemistry but also on the pore geometry.

=> To make this point clearer to the readers, we revise the manuscript as follows:

"Considering the general understanding that weaker adhesion to the pore surface accelerate the diffusion of the guest molecules in the pores,[24] we presumed that the pores in **VPC-1** is less affinitive to H_2O and can accelerate the transportation of H_2O in the pores."

(main text, page 9, line 22)

p2 line 30: Did you mistake "sutained" for "sustained"?

=> Thank you very much for pointing out our typo. We revise the word correctly.

p6 line 117: I'm curious about the structural stability of the VPC-1 against water. The XRD patterns of the VPC-1 before (0%RH) and after dehumidification should be shown. It would be even better if authors show the XRD pattern after the several repeated tests.

=> Thank you for your comment. We conducted PXRD measurements of pristine powder of **VPC-1** and the powder after ten cycles of H_2O adsorption and desorption. The PXRD profiles of both conditions show negligible difference, supporting the structural stability of **VPC-1** against water.

=> We revise the manuscript to include this result as follows:

"The PXRD profiles also revealed the structural stability of **VPC-1** against H_2O. The PXRD profiles of **VPC-1** showed negligible change even after 10 cycles of H_2O adsorption and desorption (Figure S14)."

(main text, page 9, line 13)

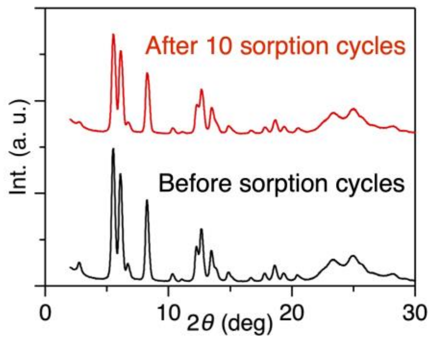


Figure S14. PXRD profiles of VPC-1 before (black curve) and after (red curve) 10 cycles of H_2O adsorption and desorption.

p8 line 148-150: Total water adsorbed amount on VPC-1, activated carbon and silica gel should be shown.

=> Thank you for your comment. We measured the sorption and found that the total water uptakes of **VPC-1**, activated carbon, and silica gel are 106.4, 473.7, and 481.1 mL(STP) g^{-1}, respectively.

=> These data are written in the revised manuscript as follows:

"In comparison to the maximum H_2O uptake of **VPC-1** (6.3 wt%, 106.4 mL(STP) g^{-1}), both silica gel and activated carbon are known to feature larger H_2O uptake (20–65 and 16–40 wt%) according to literature[27,28,29,30,31,32], which we confirmed by ourselves using the pore & surface analyzer. The experimental values for silica gel and activated carbon used for the actuation experiments were 473.7, and 481.1 mL(STP) g^{-1}."

(main text, page 19, line 2)

p9 line 171-172: Does irradiation of the laser induce structural change of VPC-1. Or is the structural changes induced by increase of temperature of the powder and/or water molecules? It is not clear whether the temperature increase of water molecule induces the desorption of water or structural changes of VPC-1 induces the desorption.

=> Thank you for your question on the cause of the desorption of water. We think it is the temperature increase of the powder that induces the desorption based on the data in Figure 3d. The plot of the temperature of **VPC-1** under irradiation of laser with a power of P_{th} (Figure 3d) is nearly constant regardless of the wavelength of the laser. This indicates that the laser warms up the powder of **VPC-1** photothermally, and H_2O desorbs when the temperature exceeds a certain limit.

=> The explanations about this issue were written in the original manuscript (page 12, lines211–215) and is written in the revised manuscript as follows:

"We found that the temperature at P_{th} (T_{th}) was nearly constant at 26.2 °C regardless of λ

of the incident light (Figures 3d, blue circles). Consequently, we concluded that the pump light increased the temperature of **VPC-1** via photothermal effect and induced the release of water, whose wavelength-dependent efficiency was affected by the absorption coefficient of **VPC-1**."

(main text, page 15, line 8)

p10 line 182-183: From which figure can we know the threshold energy is 2.1 mJ cm-1? Explain the meaning of the threshold energy (Eth) clearly.

=> Thank you for your comment on E_{th}. We draw two regression lines at lower and higher region of E and define E_{th} as the E value at the crossing point.

=> It is our fault that the value 2.1 mJ cm^{-2} written in the original manuscript was wrong. The correct E_{th} value calculated from Figure 2b is 67 mJ cm^{-2}.

=> We add the definition of E_{th} to the revised manuscript and correct the value as follows:

"the rise in diffuse reflectance became steeper when E exceeded a threshold (E_{th}) at 67 mJ cm^{-2} (Figure 2b). Here, E_{th} is defined as the E value at the crossing point of the two regression lines obtained from the data points at lower and higher E, respectively."

(main text, page 12, line 9)

p10 line 186-188: Water molecules also absorb IR. Is this IR spectrum in Fig.2c measured under vacuum or at a specific humidity? And how large is the temperature increase of the sample upon the samples?

=> The IR spectrum in Figure 2c was taken at 59.4%RH after the calibration of the absorption by the water in the atmosphere.

=> We cannot measure the temperature of the sample during the irradiation of IR pulses due to technical difficulties with the sample chamber. We designed a sample chamber that can be installed in the IR facility, but it was technically difficult to integrate thermometer within the power specimen. To visualize the configuration of the sample chamber, we newly added a detailed schematic illustration as Figure S16 to the revised manuscript. As shown therein, the sample space is thin, and the chamber is totally sealed except the inlet and outlet for the vapor. Therefore, it is technically difficult to embed the sensor tip into the power of **VPC-1** in the steel chamber.

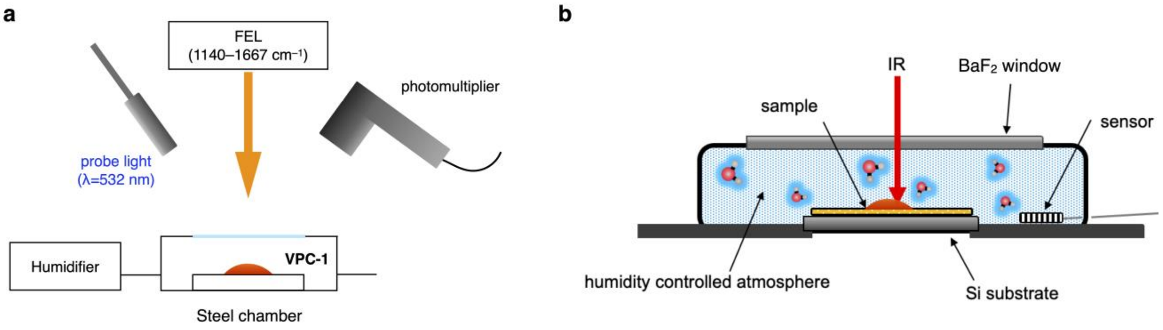


Figure S16. (a) Schematic illustration of the experimental setup for measuring diffuse reflectance of **VPC-1**, which was pumped with the infrared light generated from the free electron laser. (b) Detailed schematic illustration of the chamber.

The meaning of the sentence “,which proceeded more efficiently when exciting intense IR absorption band of G2DBPHZ” cannot be understood. Proceed what? If authors intended “the photothermal heating is proceeded more efficiently”, please correct the sentence into “,which is proceeded more efficiently when exciting intense IR absorption band of G2DBPHZ”.

=> Thank you for your comment on the grammar. The word “proceed” is an intransitive verb, and therefore we think that “proceed” should not be used in the passive voice. To avoid this grammatical discussion and to make the contents clearer to the readers, we revise the manuscript as follows:

“The energy of IR light was absorbed more efficiently, and the powder was heated more intensely when exciting intense IR absorption band of **G2DBPHZ**, inducing the H_2O desorption even at smaller *E*.”

(main text, page 12, line 16)

p11 Figure 3d: The left vertical axis label should be written as “Pth (mW cm-2)” and the right as “Tth (mW cm-2)”. Author should explain briefly what are Pth and Tth in the figure caption.

=> Thank you for indicating the misleading expressions in the figure. We revised Figure 3d and its legend as follows:

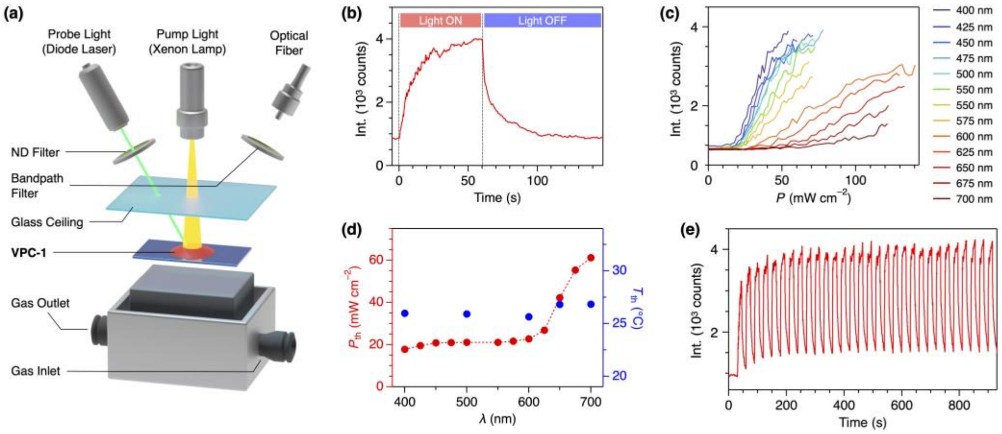


Figure 3. (a) Experimental setup for measuring moisture release from **VPC-1** based on the diffuse reflectance. (b) Time-course change in diffuse reflectance of **VPC-1**. The pump light ($\lambda = 500$ nm, $P = 80.2$ mJ cm^{-2}) was turned on at $t = 0$ s and was turned off at $t = 60$ s. (c) Diffuse reflectance of **VPC-1** as a function of *P* and λ of the pump light. (d) A plot of the threshold *P* (P_{th}) as a function of λ of the pump light (red circles),

at which is **VPC-1** started to desorb H_2O. Together with the plot of P_{th}, the temperature of **VPC-1** at P_{th} (T_{th}) of **VPC-1** is also plotted (blue circles). (e) Time-course change in diffuse reflectance of **VPC-1** when turning on the pump light for 15 s and off the light for 15 s repeatedly.

p11 line 186-188: Explain the threshold power (Pth) clearly.

=> Thank you for your comment on P_{th}. We add the definition of P_{th} in the revised manuscript as follows:

"We define the threshold power (P_{th}) as the power at the crossing point of the two regression lines obtained from the lower and higher power regions, respectively."

(main text, page 14, line 5)

p12 line 213-215: Why the authors consider only the temperature effect of visible light and why did not show the temperature increase by IR?

=> Thank you for your comment, but we cannot measure the temperature of sample during the IR experiments due to a technical difficulty. We would like to emphasize that the installation of thermometer to probe the sample temperature is technically difficult. The source and facility for generating visible light and IR pulses are totally different. The visible light is generated from a portable light source with a dimension of approximately 40 x 50 x 30 cm, and the light can be guided using an optical bundle fiber. On the other hand, the IR pulses are generated from free electron laser that occupies a whole house with a dimension of roughly 10 x 10 x 10 m. The experimental setup is mostly prefixed by the manager of the facility, and we do have so much freedom in customizing the sample chamber. We designed a sample chamber that can be installed in that facility. To visualize the configuration of the sample chamber, we newly added a detailed schematic illustration as Figure S16 to the revised manuscript. As shown therein, the sample space is thin, and the chamber is totally sealed except the inlet and outlet for the vapor. Therefore, it is difficult to embed the sensor tip into the power of **VPC-1** in the steel chamber.

=> Nonetheless, we think that it is the heat generated by the IR irradiation that causes the desorption of H_2O. As written in the original manuscript (page 10, lines 183–188), we excited **VPC-1** with variable wavenumber with an expectation that the IR excitation of some of the molecular vibrational bands may cause structural change and subsequent significant H_2O desorption. However, what we found is that E_{th} is correlated merely with the IR absorbance of the excited IR band rather than the vibrational mode. This result indicates that the IR pulses are absorbed by **VPC-1**, generate heat, and induce the H_2O desorption.

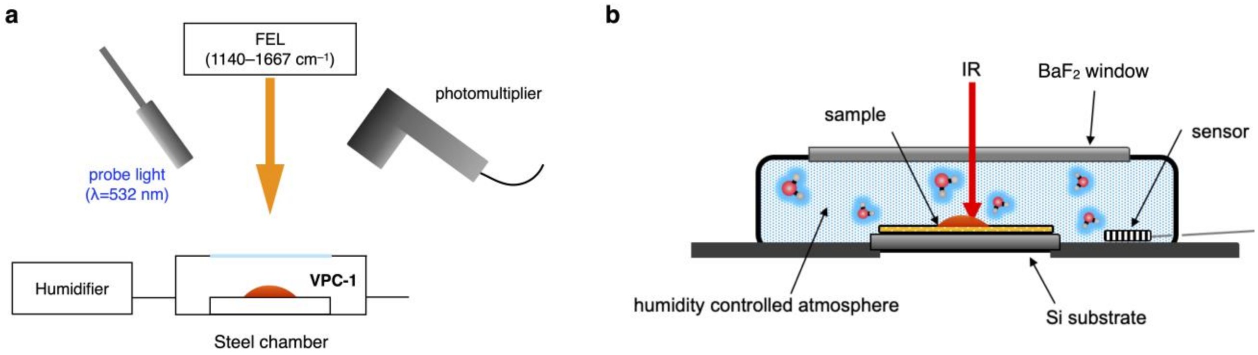


Figure S16. (a) Schematic illustration of the experimental setup for measuring diffuse reflectance of **VPC-1**, which was pumped with the infrared light generated from the free electron laser. (b) Detailed schematic illustration of the chamber.

p12 line 224-229: Why do authors choose a method using a cellophane film for detection of the quick release of water? For quantitative analysis, quartz crystal microbalance method or other methods can be applicable. The attempt using this material for a humidifier looks good and it is no doubt the VPC-1 shows the rapid adsorption and desorption behavior and this system can be applicable to an actuator. However, quantitative results containing the amount of water adsorbed/desorbed and time should be provided to justify the superiority of this material than the other materials (activated carbon and silica gel).

=> Thank you for your comment on the quantity of H_2O desorbed from **VPC-1**. A partial answer to your question on the quantitative measurements of the H_2O sorption kinetics measured with a sorption analyzer were provided as Figure S6 in the original manuscript. (original manuscript, page 30)

In addition to those, as an answer to another referee, we newly measured H_2O adsorption kinetics of activated carbon specialized for neutral gaseous molecules (UES Co., Ltd., USG-CT-S-200), multi-walled carbon nanotubes (TCI, C2155) as a totally hydrophobic porous carbon, and zeolite (zeolite A-5) as shown in Figure S15. The profile of **VPC-1** is clearly distinct from the others in that the curve shows a drastic drop just after introducing the H_2O vapor. The half decay periods of the H_2O pressure observed for **VPC-1**, carbon nanotubes, activated carbon specialized for neutral gaseous molecules, and zeolite are 1.5, 7.7, 21.0, and 14.0 sec. The activated carbon listed in the original manuscript (UES Co., Ltd., USG-PT-SX-200) was designed for capturing common gasses according to the product specifications and showed half decay periods of 9.6 sec. Except **VPC-1**, carbon nanotubes showed the fastest sorption kinetics, which is consistent with our claim that the hydrophobic pore accelerates the H_2O sorption. Please also note that the actual time constant for **VPC-1** based on the optical measurement is 490 μs, which is too fast to be measured with the specific surface area & pore size analyzer.

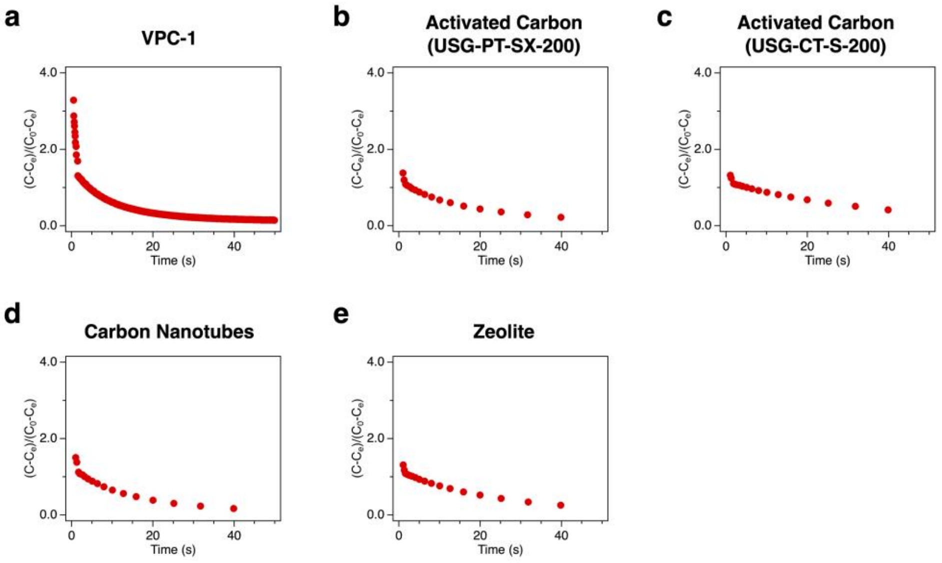


Figure S15. Time-course profile of $(C – C_e) / (C_0 – C_e)$ at 25 °C when introducing H_2O vapor to **VPC-1** (a), activated carbon for common gas (UES Co., Ltd., USG-PT-SX-200) (b), activated carbon for neutral gas (UES Co., Ltd., USG-CT-S-200) (c), carbon nanotubes (d), and zeolite A-5 (e). C is the concentration of water vapor, C_0 is the concentration of water vapor at $t = 0$ s, and C_e is the concentration of water vapor at equilibrium.

=> We were also curious about the weight loss due to the release of H_2O during the irradiation of laser and tried to measure it by using a conventional balance since the change in weight was estimated to be large according to the sorption isotherms. However, we were unable to get reliable data because photothermal heating deviated the weight value.

As a reviewer only material, the time-course change in weight (Δwt) of 1.7620 mg of **VPC-1** during the irradiation of laser ($\lambda = 400–700$ nm, $P = 0–160$ mW cm^{-2}) is shown below as Figure A. The ambient humidity and temperature were 65.4 RH% and 25.1 °C. When using blue light, the decrease in weight in the region of P larger than 100 mW cm^{-2} exceeds 10 wt%. This value is unreasonable judging from the adsorption isotherms showing maximum H_2O uptake of 3.6 wt%. We attributed the unreasonably high weight loss to the photothermal heating and associated decrease in weight. The deviation of the weight values due to the change in temperature is common for balances including quartz crystal microbalance. Therefore, we resigned to use the balance for the evaluation of the H_2O desorption.

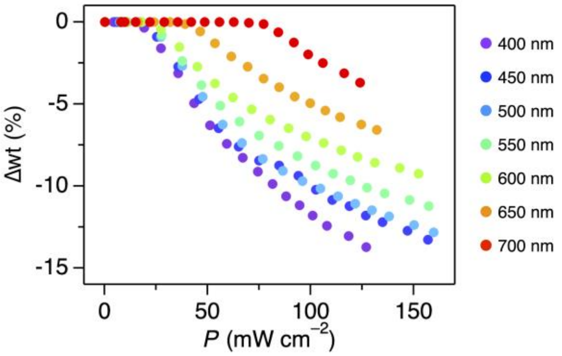


Figure A. The change in weight of **VPC-1** when irradiating visible light with variable P and λ.

=> Instead of the direct quantification of H_2O desorbed from **VPC-1**, we characterized the quantity based on the adsorption isotherms and the change in diffusion reflectance. The temperature of **VPC-1** increases from 22.6 to 35.0 °C upon irradiation of laser (λ = 500 nm) with P of 80.2 mJ cm^{-2} and desorbs 2.08 mmol of H_2O per 1 g of **VPC-1** at 60 %RH according to the H_2O isotherm curves (Figure S12) due to the decrease of the relative humidity to 29 %RH at 35.0 °C. Half of the H_2O desorption completed in 13 sec according to Figure 3b. We think these data are sufficiently quantitative to discuss the desorption induced by the light irradiation.

=> We revise the manuscript to include the quantitative analysis as follows:

"The H_2O desorption kinetics is calculated quantitatively based on the change in temperature and adsorption isotherm in Figure S12. The temperature of **VPC-1** increases from 22.6 to 35.0 °C upon irradiation of laser (λ = 500 nm) with P of 80.2 mJ cm^{-2} and desorbs 2.08 mmol of H_2O per 1 g of **VPC-1** at 60 %RH according to the H_2O isotherm curves (Figure S12) due to the decrease of the relative humidity to 29 %RH at 35.0 °C. Half of the H_2O desorption completed in 13 sec according to Figure 3b. "

(main text, page 15, line 15)

p15 line 251-253: Could you also show the time-course change in the height of the film edge (similar to Fig.4c) of activated carbon? The slow adsorption/desorption behavior should provide a slow move of the film. Then, authors can discuss which material is suitable for a humidifier and an actuator.

=> Thank you for your comment on the film actuation. We add the time-course change of the film when using activated carbon as Figure S26. The actuation by activated carbon is slower than that of **VPC-1**. To quantitatively evaluate the actuation speed, we defined the time constant of actuation as the time required for the film to reach 50% of its maximum height. Activated carbon induces the bending with a time constant of 6.8 sec, while that of **VPC-1** is 3.4 sec.

=> We revise the manuscript to include this content as follow:

"The actuation speed is also slower. To quantitatively evaluate the actuation speed, we define the time constant of actuation as the time required for the film to reach 50% of its maximum height. Activated carbon induces the bending with a time constant of 6.8 sec (Figure S26), while that of **VPC-1** is 3.4 sec."

(main text, page 19, line 16)

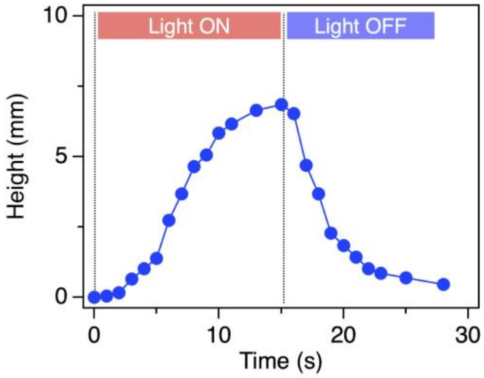


Figure S26. Time-course change in the height of film edge when irradiating activated carbon with the pump light.

p15 line 256-258: Why does the desorption of water molecules from the activated carbon decrease by repeating? Did the structure of the activated carbon change by right irradiation? Sample information of activated carbon and silica gel has to be described in the experimental section.

=> Thank you for your comment. We assume that the re-adsorption of H_2O does not complete within the interval (45 sec) between each cycle. This is in line with the slower H_2O sorption kinetics of activated carbon.

=> We revise the manuscript to include this content as follow:

"The decline in the film actuation ability is likely attributed to the slower H_2O adsorption kinetics and associated incomplete H_2O uptake within the interval (45 sec) between each cycle."

(main text, page 19, line 14)

p16 line 276: Correct "humification" into "humidification".

=> Thank you for pointing out our typo. We correct the word in the revised manuscript.

p25 line 510-512: Pre-treatment condition before adsorption measurement should be mentioned.

=> Thank you for your comments on the experimental methods. We revised the method sections to include the experimental procedures of the adsorption measurements as follows; "**VPC-1** was degassed at 50°C for at least 24 h prior to the measurements. The adsorption rates were evaluated at 25 °C by monitoring the time-dependent change in pressure after the introduction of a fixed volume of H_2O vapor into the sample chamber, using the BELSORP

MAX application.”

(supplementary information, page 29, line 6)

p33 line 633 (figure caption of Fig. S11): make space between 22.6 and °C.

=> Thank you for pointing out our typo. We correct the word in the revised manuscript.

Point-to-Point Responses to the Reviewer's Comments

For Reviewer #3:

The authors have revised the manuscript to my satisfaction. I recommend publication in Communications chemistry.

=> Thank you for your appreciation for our revisions and recommendation for publication.

I have only one comment on the part below. Are the values for AC and silica gel in the revised manuscript the opposite? The author should check the water adsorbed amount on AC and silica gel in the revised manuscript.

p8 line 148-150: Total water adsorbed amount on VPC-1, activated carbon and silica gel should be shown.

=> Thank you for your comment. We measured the sorption and found that the total water uptakes of VPC-1, activated carbon, and silica gel are 106.4, 473.7, and 481.1 mL(STP) g–1, respectively.

=> These data are written in the revised manuscript as follows: "In comparison to the maximum H2O uptake of VPC-1 (6.3 wt%, 106.4 mL(STP) g–1), both silica gel and activated carbon are known to feature larger H2O uptake (20–65 and 16–40 wt%) according to literature27,28,29,30,31,32, which we confirmed by ourselves using the pore & surface analyzer. The experimental values for silica gel and activated carbon used for the actuation experiments were 473.7, and 481.1 mL(STP) g–1." (main text, page 19, line 2)

=> Thank you for your comments. The values were mistakenly written in the main text. We have revised the manuscript as follows: "The experimental values for silica gel and activated carbon used for the actuation experiments were 481.1, and 473.7 mL (STP) g^{-1}. "