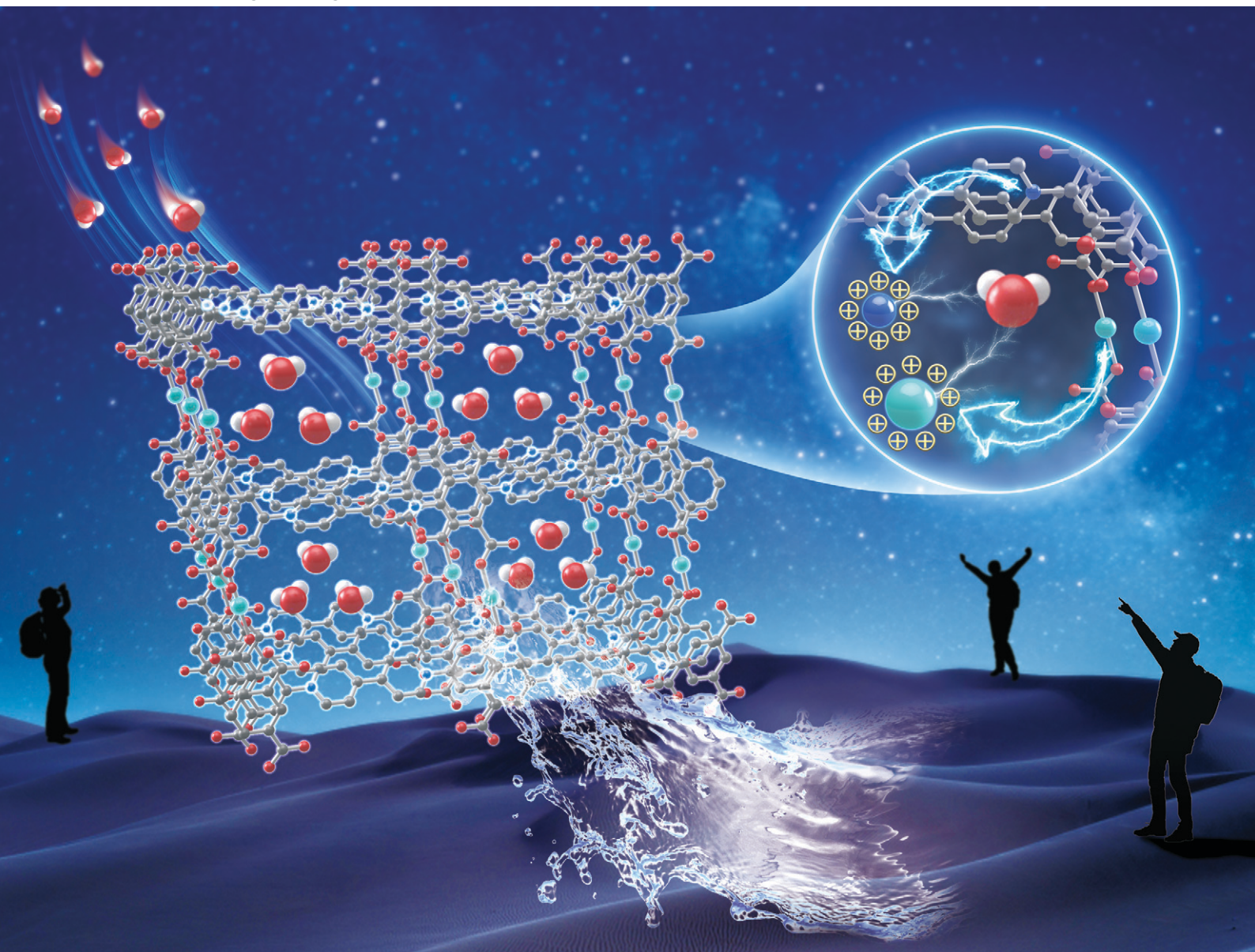


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Water harvesting properties of a zwitterionic metal–organic framework†

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Due to the rising scarcity of clean water in arid climates, there is an increased relevance in accessing clean and renewable water resources. One such perspective method, sorption-based atmospheric water harvesting, collects atmospheric water as an alternative to ground and surface water. Metal–organic frameworks (MOFs) are proposed as excellent porous materials for the capture and storage of small molecules, including water, owing to their large pore volume, high surface area, and chemical and structural tunability. Here a zwitterionic MOF (Ni-ZW-MOF), [Ni(dcpb)(H₂O)₄·14H₂O]_n, was synthesized and studied for its water sorption performance, displaying selective water adsorption and desorption capabilities. Respective sorption properties were tested in controlled low and high humidity environments over multiple cycles, demonstrating its regenerative ability and high working capacity (126.4 mL kg⁻¹ per cycle).

Introduction

Over 70% of the Earth's surface is covered in water, although only about 2.5% of those water sources are freshwater and even less are accessible drinking water resources.¹ As of 2020, over half of the world's population experiences water stress for at least one month every year, with this number expected to continue rising.^{2–4} With these problems comes the need for designing systems to provide clean renewable drinking water to water stressed areas.^{5,6} Atmospheric humidity is a significant source for freshwater in both desert and tropical

Design, System, Application

Direct air capture of water in dry climates has attracted attention by researchers due to the increasing need for reliable and affordable clean water resources. Traditional atmospheric harvesting methods, including fog and solar water capture technologies, require high relative humidity (RH), limiting accessibility to arid climates, with RH as low as 10%. In addition, water harvesting from air often requires extensive materials and energy intensive condensers to harvest adequate volumes of water. Metal–organic frameworks (MOFs) have previously been proposed as excellent sorbents for the design of advanced water harvesting systems. Due to their porous nature, MOFs are able to capture and desorb small molecules, including water, with high efficiency and capacity. In this work, a water saturated MOF is investigated for its water harvesting ability demonstrating its high adsorption capacity owing to its vast hydrogen bonding network. The designed MOF harvester shows selectivity toward water adsorption and provides insights toward the next generation of water harvesting systems for clean, renewable applications.

climates, and may be accessed through water harvesting.⁷ Many methods exist for harvesting water from humid climates, including fog and solar water collectors, but high relative humidity (RH) is a requirement for efficient performance.^{8,9} Arid regions often have day–night cycles of RH between 10–40%, significantly lower than necessary conditions for traditional water collectors. Previously, metal–organic framework (MOF) adsorption-based water harvesters have been investigated for their performance in arid climates.^{10–16}

MOFs are nanoporous, crystalline materials constructed from the self-assembly of metal ions or clusters and polytopic organic ligands. MOFs were first reported before the start of the 21st century, and have since gained traction due to their advanced performance in adsorption applications.^{17,18} This enhanced performance is due to their high internal surface areas and pore volumes in addition to their customizable structures from the large availability of metal–ligand combinations. Many water stable MOFs have been previously reported for their water harvesting potential, but zwitterionic

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† Electronic supplementary information (ESI) available: General methods, experimental procedures for MOF and ligand synthesis including ligand synthesis scheme and NMR, additional TGA data, water isotherm, crystallographic tables of MOF including refinement and geometrical parameters, and ORTEP plot. Crystal structure data has been deposited to the Cambridge Crystal Structure Database with CCDC number 2220643. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d2me00284a>

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ligand-based MOFs have yet to be investigated for their water adsorption performance.^{19–22}

Zwitterions are molecules featuring both positive and negative charges from present functional groups (*e.g.*, pyridinium and carboxylates).^{23,24} If used for MOF synthesis, these ligands can generate charged-polarized pore environments which have the potential to induce strong host-guest interactions of polarizable guest molecules. For example, bipyridinium-based carboxylate ligands possess quaternary ammonium salts which can act as Lewis acid sites, increasing affinity for adsorption of water molecules.

In this work, a nickel-based zwitterionic MOF, $[\text{Ni}(\text{dcpb})(\text{H}_2\text{O})_4 \cdot 14\text{H}_2\text{O}]_n$ (Ni-ZW-MOF), composed of a tetratopic bipyridinium carboxylate ligand ($\text{H}_4\text{dcpb} \cdot 2\text{Cl} = 1,1'$ -bis(3,5-dicarboxyphenyl)-4,4'-bipyridinium dichloride) featuring accessible hydrogen bonding sites and coordinated and non-coordinated water molecules, is studied for its water sorption performance in arid and humid environments. The activated MOF possesses two Lewis acid sites which includes a node-based open Ni^{2+} site and a ligand-based pyridinium moiety and exhibits hydrochromic behavior providing visual indication of the water harvesting process. Static and dynamic water adsorption experiments were conducted to investigate the Ni-ZW-MOF's ability to harvest water from air in low and high humidity conditions.

Results and discussion

Crystals of Ni-ZW-MOF were obtained from a reaction of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and the ZW ligand $\text{H}_4\text{dcpb} \cdot 2\text{Cl}$ in an equivalent mixture of DMF/ H_2O using dicyandiamide as a modulator. Experimental details of the MOF and ligand synthesis are provided in the ESI.† Single crystal X-ray diffraction analysis revealed that Ni-ZW-MOF crystallizes in the monoclinic space group $C2/c$ with the asymmetric unit composed of a half $\text{Ni}(\text{II})$ metal center, half dcpb ligand, two coordinated water molecules, and seven lattice water molecules. Fig. S2† displays the corresponding ORTEP plot at 50% electron density probability level. The $\text{Ni}(\text{II})$ centers are octahedrally coordinated by six O atoms of two monodentate dcpb ligands and four water molecules (Fig. 1a). These octahedral nodes are bridged by dcpb ligands into 1D zigzag chains which are represented in Fig. 1b and c along the crystallographic *b*- and *c*-axis, respectively. Non-coordinating carboxyl groups of the dcpb ligand allow lattice water molecules to interconnect those chains through hydrogen bonding interactions into a 3D supramolecular framework. Respective hydrogen bonds are listed in Table S7.† This structural arrangement results into the formation of 1D channel pores ($9.6 \times 11.5 \text{ \AA}^2$) along the crystallographic *b*-axis which are filled by 14 non-coordinating lattice water molecules per formula unit as shown in Fig. 1d.

The thermal behavior of Ni-ZW-MOF was investigated using thermal gravimetric analysis (TGA) under a nitrogen atmosphere. From the full temperature profile ranging 20–800 °C as shown in Fig. 2a it is evident that the MOF

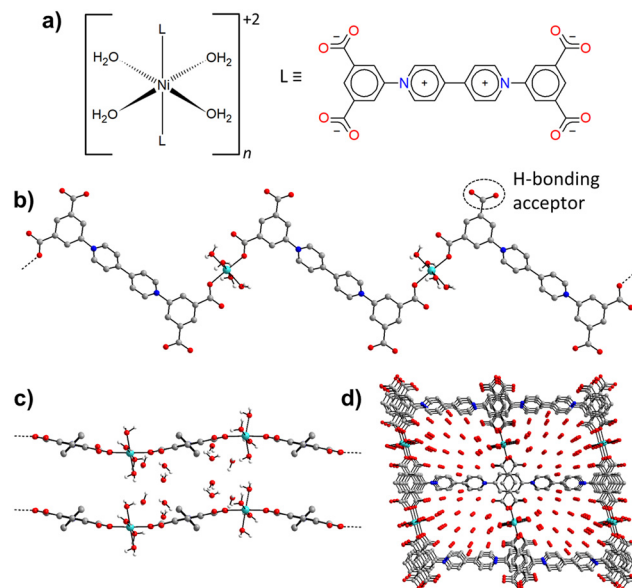


Fig. 1 Crystal structure of Ni-ZW-MOF. a) Octahedral coordination environment of Ni^{2+} cations with L representing the ZW ligand dcpb; 1D zigzag chains shown along the crystallographic b) *b*-axis and c) *c*-axis; and d) packing diagram along the crystallographic *b*-axis. Aromatic hydrogens and disorder are omitted for clarity; grey-carbon, blue-nitrogen, red-oxygen, cyan-nickel.

dehydrates upon heating to 100 °C followed by decomposition starting around 300 °C. The initial mass loss step totals around $\Delta m_{\text{exp}}(20 \rightarrow 100 \text{ °C}) = 29.3\%$ which is less than one would expect for the removal of 18 water molecules as calculated from SCXRD data $\Delta m_{\text{cal}}(-18\text{H}_2\text{O}) = 38.0\%$. This deviation is no surprise given that some volatile lattice water molecules might have evaporated during vacuum filtration of the sample in preparation for the TGA measurement. The initial heating step can be separated into two consecutive events on closer examination of the <100 °C region as detailed in Fig. 2b. The first derivative of the TGA curve is also plotted as reference to indicate the inflection points of each step in the dehydration process. The first step with $\Delta m_{\text{exp}}(20 \rightarrow 60 \text{ °C}) = 20.5\%$ and second step with $\Delta m_{\text{exp}}(60 \rightarrow 100 \text{ °C}) = 8.8\%$ can be assigned to the removal of about ten lattice and four coordinating water molecules, respectively. This two-step process matches well with the expected binding behavior of the two types of water molecules in the structure. The lattice water molecules only weakly interact with the MOF, evident from their fast removal kinetics, while the coordinated water molecules interact strongly with Ni^{2+} binding sites, delaying their removal process.

The thermal water removal process was further monitored through powder X-ray diffraction (PXRD) as displayed in Fig. 2c. After activation of Ni-ZW-MOF at 120 °C for 1 h, the PXRD shows no reflections (blue pattern), indicating the formation of an amorphous phase. It can be assumed that the loss of a combination of lattice and coordinated water molecules leads to structural deformities from the changing coordination environment of Ni^{2+} .²⁵ Two additional

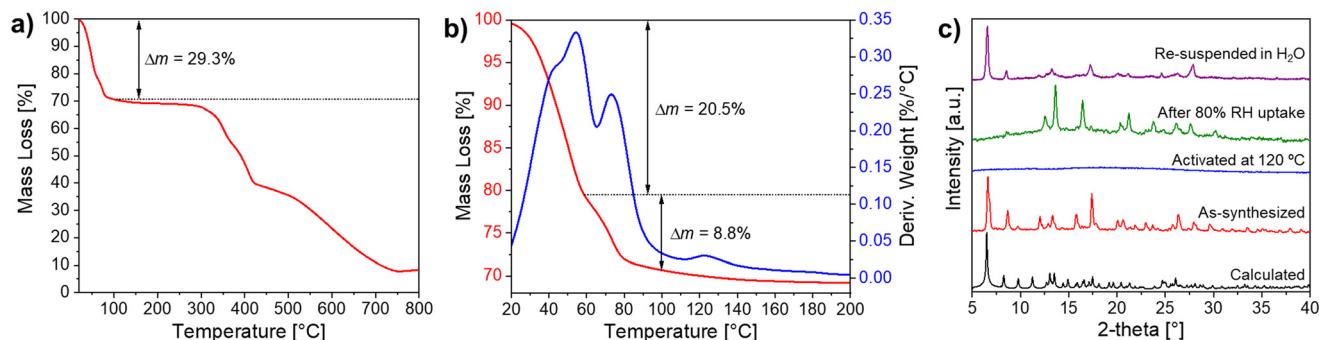


Fig. 2 Thermogravimetric and PXRD characterizations of Ni-ZW-MOF. a) Full TGA profile under N_2 atmosphere ranging 20–800 °C; b) TGA (red) and DTG (blue) profiles in the <200 °C range; and c) PXRD analysis after different water adsorption and desorption processes.

experiments were performed to investigate the MOF's crystallinity upon rehydration. First, the amorphous fully dehydrated sample was exposed to a controlled 80% RH atmosphere for 2 h. From the respective PXRD (green pattern) it is evident that the sample regains crystallinity although the Bragg reflections do not match to the original as-synthesized phase (red pattern), indicating the formation of a new crystalline phase formed under humid conditions. Second, another dehydrated sample was fully immersed in water for 2 h. The PXRD of the resulting rehydrated sample (magenta pattern) shows reflections matching Bragg positions with the original pristine phase but different reflection intensities, indicating that the dehydration process is reversible. Observing changes in the reflection intensities is no surprise given that the de- and rehydration process causes defects within the macroscopic crystal lattices. Both rehydrated samples were further investigated by TGA showing that the samples from first and second experiments contain about 6.3 (one mass loss step, 13.2%) and 14.4 water molecules/formula unit (two mass loss steps, total 30.4%), respectively. Respective TGA profiles are shown in Fig. S3.†

Based on the above TGA and PXRD data, the mechanism for thermal activation, water capturing and water harvesting of Ni-ZW-MOF is proposed in Fig. 3. The thermal activation

process occurs in two steps as the as-synthesized material $[Ni(dcpb)(H_2O)_4 \cdot 14H_2O]_n$ first loses the lattice water molecules forming a new crystalline intermediate phase of composition $[Ni(dcpb)(H_2O)_4]_n$ followed by full dehydration to form an amorphous anhydrate of composition $[Ni(dcpb)]_n$. Notably, however, the intermediate phase can only be obtained from partial rehydration of the anhydrate and cannot be directly isolated from thermal activation of the as-synthesized form. Any structural rearrangements during these de- and rehydration processes are best depictable through changes of interchain distances along the crystallographic *c*-axis. For the as-synthesized phase as shown in Fig. 3a, lattice and metal-coordinating water molecules occupy the interchain voids aiding the formation of a 3D supramolecular interchain framework stabilized by strong intermolecular hydrogen bonding interactions. Followed by full thermal dehydration, all stabilizing H-bonding interactions diminish and consequently all long-range order of the interchain framework collapses leading to the formation of a close and irregular packed amorphous compound as illustrated in Fig. 3b. Herein, the Ni^{+2} cations act as Lewis acid sites where the water molecules were initially coordinated.²⁶ Upon exposure to humid air, metal-coordinating water molecules can be reintroduced into the

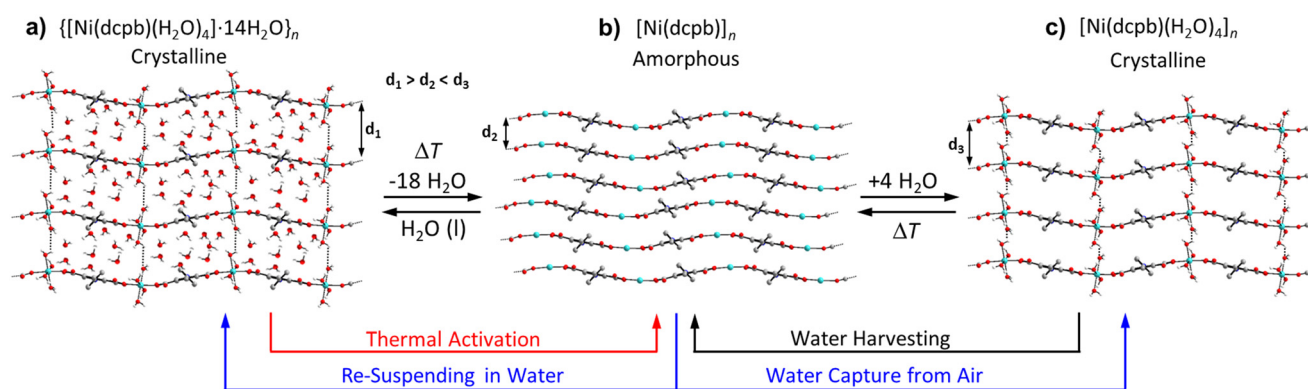


Fig. 3 Schematic representation of structural changes during thermal activation, water capturing and water harvesting of Ni-ZW-MOF shown along the crystallographic *c*-axis. Aromatic hydrogens and disorder are omitted for clarity; dashed lines represent H-bonding; grey-carbon, blue-nitrogen, red-oxygen, cyan-nickel.

amorphous interchain framework allowing the framework to recrystallize *via* the formation of interchain H-bonding interactions. Given the absence of any lattice water molecules at this stage as depicted in Fig. 3c, interchain distances of this new crystalline intermediate phase are assumingly shorter as compared to the fully hydrated form. It can be assumed that there is not sufficient critical mass of water molecules in humid air for the sample to return to the as-synthesized phase. However, filling the interchain voids with lattice water molecules becomes possible upon resuspending the sample in water which eventually transforms the intermediate phase into the as-synthesized form. A similar transformation can be observed when the fully activated anhydrate form is directly resuspended in water. A water adsorption isotherm was obtained to support this mechanism. The isotherm in Fig. S4† shows a two-step adsorption process, corresponding to the coordination of water molecules to the metal center followed by adsorption into the pores at very high relative humidity. The adsorbed water molecules can then be harvested through a thermal reactivation process of the material. As probed below, this process of water capturing and harvesting has the potential to be cycled in order to create a water harvesting system.

During the above experiments, it was observed that Ni-ZW-MOF possesses hydrochromic properties. Previous investigations discussed Ni-ZW-MOF as a photochromic

material.²⁷ Hydrochromic behavior of viologen ligands is infrequently discussed in the literature, owing to the unique and rare occurrence.^{25,28,29} Hydrochromism occurs as a result of free radical formation *via* electron transfer of the bipyridinium ligand during the dehydration process. Transition metal complexes more commonly exhibit hydrochromic behavior from d-d transitions within the ligand field during the desorption-adsorption process of the water molecules.^{25,30-32} The hydrochromic behavior was monitored through diffuse reflectance spectroscopy (DRS) as shown in Fig. 4a. The as-synthesized Ni-ZW-MOF exhibits a color change from yellow to dark green after thermal activation (Fig. 4b and c). The color transition can be observed from an increase in the absorbance spectra of the red region (650 nm) between the yellow as-synthesized Ni-ZW-MOF crystals and the green thermally activated material.

Based on the hygroscopicity of Ni-ZW-MOF, static and dynamic water adsorption studies were employed to investigate its water harvesting ability. Fixed isothermal adsorption tests were performed on the activated material at 30 °C in four different RH environments (10–80% RH). Per Fig. 4d, at 10% RH (red curve), an adsorption capacity of 46 mg g⁻¹ was observed after exposure to the specified conditions for 90 min. The kinetics of the adsorption process are observed to increase with higher RH, with 40% (blue curve), 50% (cyan curve), and 80% (magenta curve) reaching

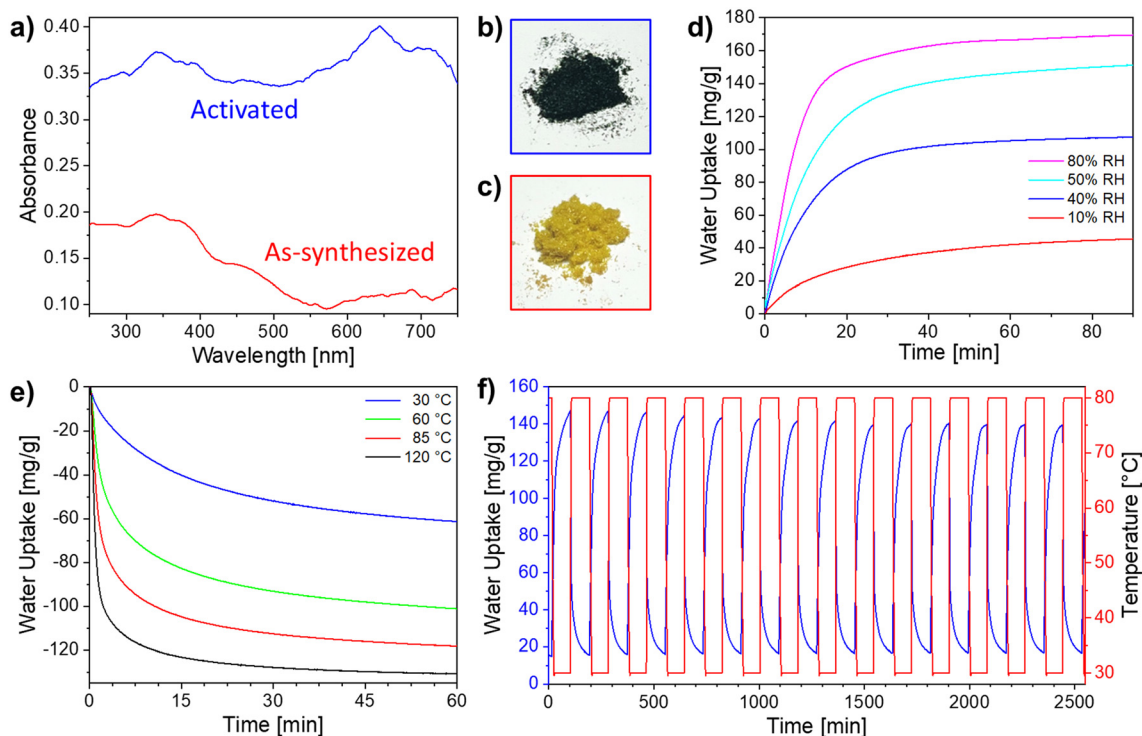


Fig. 4 a) DRS spectra of as-synthesized and activated Ni-ZW-MOF; photographs of b) thermally activated and c) as-synthesized Ni-ZW-MOF; d) water adsorption properties at 30 °C and varying % RH (after full thermal activation); e) water desorption properties at varying temperatures and 0% RH (after water adsorption at 30 °C and 45% RH); and f) temperature swing water adsorption-desorption cycles of Ni-ZW-MOF between 30 °C at 45% RH and 80 °C at 0% RH with each isothermal step hold for 90 min.

near full capacity after only 30 min. In addition, at higher RH (50% and 80%), water uptake reaches highest amounts of 151 and 170 mg g⁻¹, respectively, with only a 12% water uptake increase with a 30% RH increase. Given that the expected water uptake between the anhydrate [Ni(dcpb)]_n and the tetra-hydrate intermediate [Ni(dcpb)(H₂O)₄]_n is 136 mg g⁻¹, this data suggests that metal-coordinating water molecules are adsorbed below 50% RH and water molecules start filling the pores around 50% RH. Interestingly, this pore filling occurs into the interchain void space of the intermediate phase as depicted in Fig. 3c. Even at 80% RH the critical mass of water molecules in the gas phase is not sufficient to allow retransformation into the as-synthesized phase as evident from Fig. 2c, green PXRD. Nevertheless, these findings demonstrate that Ni-ZW-MOF has a strong ability to adsorb water even in low RH conditions.

Similarly, desorption experiments at varying isothermal temperatures and 0% RH were performed after full thermal activation followed by water adsorption at 30 °C and 45% RH. Respective dehydration behavior is plotted in Fig. 4e. As expected, faster and complete desorption is observed at higher temperatures. For all desorption temperatures tested, desorption kinetics slow down after the first 15 min. Though complete desorption is not achieved at mild desorption temperatures of 30 °C (blue curve), about half of the adsorbed water can be harvested after only 1 h. At 120 °C (black curve), complete desorption was achieved after 45 min of the isothermal process. These experiments demonstrate that Ni-ZW-MOF is able to function as a water harvesting material under mild conditions—an important prerequisite for designing systems for arid climates.

The recyclability of Ni-ZW-MOF for water harvesting was assessed through dynamic water adsorption–desorption cycling experiments as shown in Fig. 4f (adsorption conditions: 30 °C and 45% RH; desorption conditions: 80 °C and 0% RH). At mild temperatures, nearly complete desorption was achieved in 90 min (0.5 water molecules/formula unit retained) and over 14 adsorption–desorption cycles, Ni-ZW-MOF retained about 94.2% of its adsorption capacity. The sample's stability after cycling was confirmed by PXRD (Fig. S5†). On average, the observed working capacity of Ni-ZW-MOF is 126.4 mL kg⁻¹ per cycle (3.7 water molecules/formula unit) which outperforms other reported sorbents such as UiO-66 (30 mL kg⁻¹) and zeolite 13X (20 mL kg⁻¹) under similar conditions.¹⁹

Conclusions

A Ni(II)-based zwitterionic MOF (Ni-ZW-MOF) was synthesized from a tetratopic disubstituted bipyridinium ligand. The crystal structure features metal-coordinating water molecules in addition to charged-polarized 1D channel pores occupied with lattice water molecules. This water stable MOF can act as Lewis acid when thermally activated due to its open metal sites resulting from the water desorption process along with

the pyridinium functionalities of the viologen ligand. When activated, Ni-ZW-MOF can adsorb water from humid air with adsorption capacities of 45.5 mg g⁻¹ in 10% RH and 169.5 mg g⁻¹ in 80% RH environments. These capacities at low and high RH demonstrate the excellent water harvesting performance of Ni-ZW-MOF. Over multiple adsorption–desorption cycles, Ni-ZW-MOF retained 94.2% of its adsorption capacity, exhibiting an average working capacity of 126.4 mL kg⁻¹ per cycle under given conditions. From the structural features of the MOF one can conclude that the strong Lewis acidity of Ni²⁺ ions and pyridinium moieties accounts for its significant water adsorption capacity. Overall, its stability in aqueous environments and high adsorption performance at low RH, in tandem with low desorption energies and good regeneration abilities, demonstrates the excellent potential for Ni-ZW-MOF as a water harvesting sorbent in arid regions.

Conflicts of interest

There are no conflicts to declare.

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