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# Metal- and halide-free, solid-state polymeric water vapor sorbents for efficient water-sorption-driven cooling and atmospheric water harvesting†

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Metal- and halide-free, solid-state water vapor sorbents are highly desirable for water-sorption-based applications, because most of the solid sorbents suffer from low water sorption capacity caused by their rigid porosity, while the liquid sorbents are limited by their fluidity and strong corrosivity, which is caused by the halide ions. Herein, we report a novel type of highly efficient and benign polymeric sorbent, which contains no metal or halide, and has an expandable solid state when wet. A group of sorbents are synthesized by polymerizing and cross-linking the metal-free quaternary ammonium monomers followed by an ion-exchange process to replace chloride anions with benign-anions, including acetate, oxalate, and citrate. They show significantly reduced corrosivity and improved water sorption capacity. Importantly, the water sorption capacity of the acetate paired hydrogel is among the best of the literature reported hygroscopic polymers in their pure form, even though the hydrogel is crosslinked. The hydrogel-based sorbents are further used for water-sorption-driven cooling and atmospheric water harvesting applications, which show improved coefficient of performance (COP) and high freshwater production rate, respectively. The results of this work would inspire more research interest in developing better water sorbents and potentially broaden the application horizon of water-sorption-based processes towards the water-energy nexus.

## New concepts

Water vapor sorbents are the key components in various emerging water-sorption-based applications, such as sorption-based cooling/heating technologies, atmospheric freshwater harvesting, vapor-sorption-based desalination, and air humidity regulation. Most of these applications can be driven by solar energy alone, making them very promising in establishing a greener and more sustainable world. However, most of the solid sorbents suffer from a low water sorption capacity, while the liquid sorbents are limited by their fluidity and strong corrosivity. Here, for the first time, we report a novel type of metal- and halide-free, solid-state polymeric water vapor sorbents with improved water vapor sorption capacity, reduced corrosivity, and solid state when wet. To achieve this, we demonstrate a new concept to fabricate polymeric sorbents by polymerizing and crosslinking the metal-free quaternary ammonium monomers followed by an ion-exchange process to replace halide anions with benign-anions. The as-developed polymeric sorbents exhibit (1) high water vapor sorption capacity thanks to the deliquescent nature of quaternary ammonium cations and benign-anions; (2) reduced corrosivity due to the halide-free nature of benign-anions; and (3) solid state when wet due to the crosslinked structure. As such, the halide-free sorbents show improved coefficient of performance (COP) and high freshwater production rate in water-sorption-driven cooling and atmospheric water harvesting applications.

## 1. Introduction

Due to the ever-worsening global warming, increasing global population, and steady improvement of life standards, adequate

clean water and stable supply of clean energy with low carbon footprint are two key challenges for global sustainable development.<sup>1–8</sup> On the other hand, there is a vast amount of water constantly preserved in the Earth's atmosphere, generically known as atmospheric water, which is equivalent to six times all the water in all the rivers on Earth.<sup>6,9</sup> The capture-release of water vapor has underpinned a number of emerging designs significant to the water-energy nexus, such as sorption-driven heat transformation for cooling and heating,<sup>10–14</sup> atmospheric water harvesting (AWH),<sup>15–28</sup> vapor-sorption-based desalination,<sup>14,29</sup> and air humidity regulation.<sup>30,31</sup> In particular, sorption-driven cooling and AWH are gaining a lot of interest nowadays in both academia and industry as they aim at reducing electricity consumption, obsoleting the conventional harmful coolants (e.g., chlorodifluoromethane, 1,1,1,2-tetrafluoroethane),<sup>32</sup> and producing

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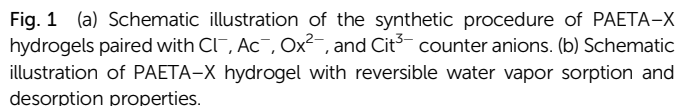
water vapor sorption capacities, and reduced metal corrosivity. The hydrogel paired with acetate (PAETA-Ac) showed an improved water uptake of  $\sim 0.31 \text{ g g}^{-1}$  at a low relative humidity (RH) of 30%, and an increased water uptake of  $\sim 0.87 \text{ g g}^{-1}$  at RH of 80%, which is the highest number for any reported polymeric water sorbents in their pure form without inorganic salt and any other additives. It is even higher than those non-crosslinked polymers like PPY-Cl ( $\sim 0.18 \text{ g g}^{-1}$ ),<sup>20</sup> PAAS ( $\sim 0.58 \text{ g g}^{-1}$ ),<sup>38</sup> and PDDA ( $\sim 0.80 \text{ g g}^{-1}$ ).<sup>45</sup> For a typical air-conditioning application, PAETA-Ac produced a coefficient of performance (COP) of 0.75 for cooling with a temperature lift of  $20^\circ\text{C}$  at a low sorbent regeneration temperature ( $\sim 70^\circ\text{C}$ ). The low regeneration temperature of the sorbent enables the use of low-grade industrial waste heat or heat generated from solar energy by simple solar-thermal conversion in both cooling and AWH applications. The outdoor field AWH experimental results showed that PAETA-Ac can produce  $\sim 0.53 \text{ g g}^{-1}$  freshwater from one cycle of water vapor sorption and desorption. All of these results show that the metal- and halide-free solid-state polymeric vapor sorbents first reported in this work have the potential to make a solid contribution to the global water-energy nexus.

## 2. Results and discussion

Recently, organic materials have been investigated as alternative water vapor sorbents because of their low-cost, less toxicity, and the wide pool of potential candidates. Hygroscopic polymers,<sup>20–22,38–46</sup> like poly(acrylic acid) sodium salt (PAAS),<sup>21,38</sup> chloride-doped polypyrrole (PPy-Cl),<sup>20,43,44</sup> sodium alginate (Alg),<sup>41</sup> poly(diallyldimethylammonium chloride) (PDDA),<sup>45</sup> *etc.*, as well as glycerin,<sup>23</sup> and ionic liquid,<sup>24,29,36,46</sup> are mostly reported. However, much like the inorganic salt-based sorbents, the non-crosslinked hygroscopic polymers, glycerin, and ionic liquid, all work in liquid form. Besides, there is a dilemma in these reported materials: the halide-free polymers possess significantly lower water sorption capacities while the halide-containing polymers suffer from strong corrosivity. Therefore, the development of metal- and halide-free, solid-state water vapor sorbents with high water sorption capacity are highly sought after.

Fig. 1a presents the synthetic procedure of the polycationic hydrogels paired with different counter anions. The PAETA-Cl hydrogel was first synthesized *via* polymerization of a quaternary ammonium-based monomer, *i.e.*, AETA-Cl, with  $N,N'$ -methylenebisacrylamide (BIS) as the crosslinking agent. After the polymerization and cross-linking, liquid AETA-Cl monomer solution (Fig. S1a, ESI<sup>†</sup>) was transformed into a solid hydrogel (Fig. S1b, ESI<sup>†</sup>). The hydrogel was flexible and could be cut into small pieces without structural collapse (Fig. S1c, ESI<sup>†</sup>). Subsequently, an ion-exchange process was conducted to exchange the  $\text{Cl}^-$  anion with acetate ( $\text{Ac}^-$ ), oxalate ( $\text{Ox}^{2-}$ ), or citrate ( $\text{Cit}^{3-}$ ) counter anions, respectively. The as-prepared polycationic hydrogels are denoted as PAETA- $X$ , where  $X$  represents the counter anion of  $\text{Cl}^-$ ,  $\text{Ac}^-$ ,  $\text{Ox}^{2-}$ , and  $\text{Cit}^{3-}$ , respectively. Since quaternary ammonium cations and carboxylate anions are well known as the deliquescent components that can attract water molecules,<sup>21,24,39,45</sup> an AETA-based cation and  $\text{Ac}^-$ ,  $\text{Ox}^{2-}$ , and  $\text{Cit}^{3-}$  are rationally chosen for the fabrication of Cl-free water vapor sorbents. The Cl-free PAETA- $X$  hydrogels can sorb water vapor from ambient air and desorb the water vapor under a low temperature or sunlight irradiation (Fig. 1b), which can be used for energy-efficient water-sorption-driven cooling and AWH applications.

Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) and energy-dispersive X-ray spectroscopy (EDS) were used to analyze the chemical composition of the synthesized hydrogels. Fig. 2a shows the ATR-FTIR spectra of PAETA-X hydrogels, where the characteristic peaks at  $\sim 1726$ ,  $\sim 1160$ ,  $\sim 1479$ , and  $\sim 950\text{ cm}^{-1}$  are due to the C=O and C-O-C stretching of esters,  $-\text{CH}_3$  bending vibration and stretching vibration of quaternary ammonium  $[\text{R}-\text{N}(\text{CH}_3)_3]^+$ , respectively.<sup>47</sup> These characteristic peaks persist in the FTIR spectra before and after



The thermal stabilities of PAETA-X hydrogels were determined by thermogravimetric analysis (TGA), and the resultant

The  $T_g$  values of PAETA-X hydrogels were also analyzed in the wet state after a 6 h water sorption process under ambient conditions. In the wet state (Fig. 2d, right), the  $T_g$  values of all PAETA-X hydrogels were reduced to below 0 °C, indicating that PAETA-X hydrogels have a rubbery state when wet. This is because water molecules penetrate into the hydrophilic polymer matrix and bind to the polar groups of the polymer chains, which weakens the interactions among the polymer chains, consequently leading to the plasticization of PAETA-X hydrogels and an increase of their molecular mobility and free volume.<sup>52</sup>

The water vapor sorption capacity of PAETA-X hydrogel with different anions was in the order of  $\text{Ac}^- > \text{Ox}^{2-} > \text{Cit}^{3-} > \text{Cl}^-$  under all RH conditions, which was presumably because after the ion-exchange process, the mobility of the polymer chains is increased and the hydrogen-bond basicity of the anions is

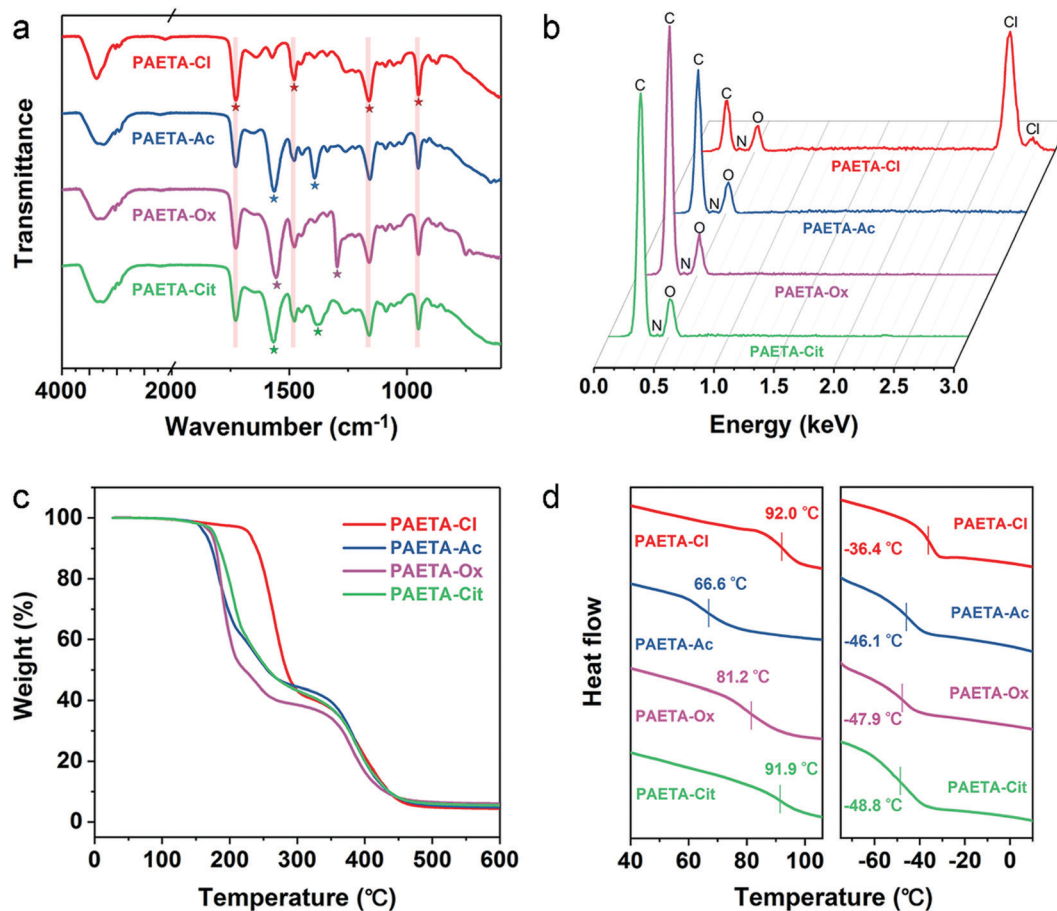


Fig. 2 (a) ATR-FTIR spectra, (b) EDS spectra, (c) TGA curves, and (d) DSC curves (left: dry, right: wet) of PAETA-Cl, PAETA-Ac, PAETA-Ox, and PAETA-Cit hydrogels.

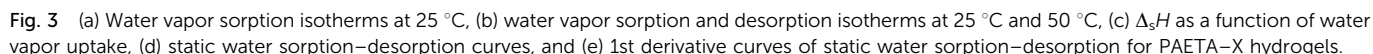
increased by introducing carboxylate ions.<sup>46,53</sup> Among all, PAETA-Ac shows the highest water sorption capacity ( $\sim 0.87 \text{ g g}^{-1}$  at 25 °C, 80% RH), higher than other metal- and halide-free polymeric sorbents reported in the literature under the same conditions, such as an epoxy-functionalized porous organic polymer (ep-POP,  $< 0.4 \text{ g g}^{-1}$ ), and a pseudoprotein-based fully organic polymeric desiccant ( $< 0.09 \text{ g g}^{-1}$ ).<sup>22,40</sup> Importantly, the water vapor sorption capacity of PAETA-Ac hydrogel is among the best in the reported hygroscopic polymers in their pure form and traditional desiccants (e.g., silica gel and zeolite), even though the PAETA-Ac hydrogel was crosslinked in this case (Fig. S3, ESI†). PAETA-X hydrogels show higher water vapor sorption capacity due to the existence of two types of highly hygroscopic groups, i.e., the quaternary ammonium group and carboxylate group.<sup>21,24,39,45</sup> Compared with other typical sorbents, although PAETA-X hydrogel shows lower water sorption capacity ( $\sim 0.87 \text{ g g}^{-1}$  at 80% RH) than some MOFs ( $\sim 0.95 \text{ g g}^{-1}$ ),<sup>54</sup> hygroscopic salts (e.g., LiCl, CaCl<sub>2</sub>,  $> 1.5 \text{ g g}^{-1}$ ),<sup>15,19,34</sup> and ionic liquids ( $> 1.0 \text{ g g}^{-1}$ ),<sup>24</sup> its advantages of halide free, facile fabrication, and solid state make PAETA-X hydrogel an attractive sorbent.

The water vapor sorption and desorption isotherms of PAETA-X hydrogels at 25 °C and 50 °C were measured (Fig. 3b), based on

which the enthalpy of sorption ( $\Delta_s H$ ) for water was calculated (Supplementary Note S1 and Eqn S1 in the ESI†). As shown in Fig. 3c, the  $\Delta_s H$  values were relatively high when the water uptake was low, due to the fact that the initial sorbed water molecules have relatively strong interactions with the polymer hydrophilic groups.<sup>24</sup> As the water uptake increased, the  $\Delta_s H$  values were gradually reduced to constant values of about  $-45 \text{ kJ mol}^{-1}$ ,  $-46 \text{ kJ mol}^{-1}$ ,  $-46 \text{ kJ mol}^{-1}$ , and  $-46 \text{ kJ mol}^{-1}$  for PAETA-Cl, PAETA-Ac, PAETA-Ox, and PAETA-Cit, respectively. The constant  $\Delta_s H$  values are close to the enthalpy of water evaporation ( $\sim 44 \text{ kJ mol}^{-1}$  at 30 °C), indicating that hydrogen bond interactions among water molecules play a dominant role therein.<sup>13,24</sup>

The water vapor sorption kinetics were evaluated by conducting a static RH test at 25 °C in a nitrogen flow with RH of 60%. The results show that PAETA-X hydrogels possess a fast vapor sorption kinetics, with the sorption equilibrium being achieved within 3 hours (Fig. 3d and e). In comparison, CaCl<sub>2</sub> liquid sorbent,<sup>19</sup> glycerin-based organogel sorbent,<sup>23</sup> IL sorbent,<sup>24</sup> CaCl<sub>2</sub>/PAM sorbent,<sup>15</sup> LiCl/CaCl<sub>2</sub>/alginate sorbent,<sup>34</sup> etc., all require more than 12 hours to reach the sorption equilibrium. In the desorption process at 70 °C,  $\sim 90\%$  of the sorbed water was released from PAETA-X hydrogels within 0.5 hour, while the





The possible structures/conformations of two PAETA-X chains (9 repeating AETA units) paired with different anions were searched using the Molclus program.<sup>56</sup> Ten initial conformations were obtained, and then xtb software was applied for their optimization, where the conformation with the lowest single point energy was considered as the most stable conformation.<sup>57</sup> The schematic diagrams of the most stable PAETA-X conformations were performed *via* VMD and Multiwfn software,<sup>58,59</sup> as shown in Fig. 4. The typical distance between the two polymer chains of PAETA-Ac (7.91 Å) is significantly larger than that of PAETA-Cl (4.80 Å). Accordingly, the small

**Fig. 4** (a) Simulated structures/conformations of the two PAETA-X polymer chains (9 repeating AETA units) that are bound together with (a)  $\text{Cl}^-$ , (b)  $\text{Ac}^-$ , (c)  $\text{Ox}^{2-}$ , and (d)  $\text{Cit}^{3-}$ . For clarity, one polymer chain is shown in red and the other in blue.

For air-conditioning applications, the evaporation temperature ( $T_{\text{ev}}$ ) was set as 10 °C and the condensation temperature ( $T_{\text{con}}$ ) was set as 30 °C (Fig. S7, ESI†) according to the literature

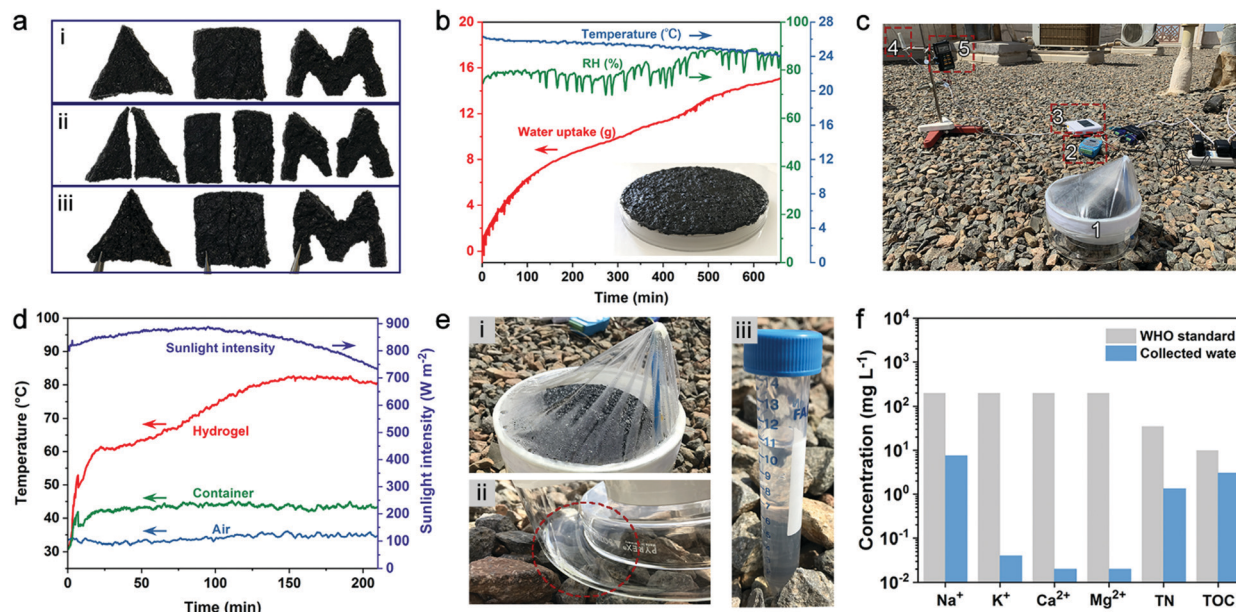


Silica gels are widely studied as the sorbents for sorption-driven cooling applications, but they show relatively low water

For practical air-conditioning applications, the PAETA-X hydrogel has the potential to be used in sorption beds by coating to the surface of the heat exchanger or integrating into porous silica gel, expanded graphite, metallic foam, and activated carbon fiber to form composite sorbents, which can be achieved through grafting, coating, or composite methods.<sup>45,61-63,68-70</sup>

The adhesion performance of a PAETA-Ac/CNT hydrogel to diverse materials was characterized by using lap shear tests,<sup>71,72</sup> where the PAETA-Ac/CNT hydrogel was sandwiched between a pair of glass slides and a pair of stainless steel sheets, respectively. The assemblies were stretched from both ends until separation or fracture. Fig. S11 (ESI<sup>†</sup>) shows representative adhesion strength-displacement curves for the PAETA-Ac/CNT hydrogel on glass and stainless steel. As can be seen, in the dry state, the adhesion strength of PAETA-Ac/CNT on the glass and stainless steel was 649.5 and 557.3 kPa respectively, which was significantly larger than that in the wet state (16.9 kPa on glass, 12.8 kPa on stainless steel, Fig. S11c and d, ESI<sup>†</sup>). This is because the hydrogen bond interactions between PAETA-Ac/CNT hydrogel and glass or stainless steel endow high adhesion strengths in the dry state. While, in the wet state, water molecules can interact with various groups of the PAETA-Ac/CNT hydrogel directly, which weakens the interactions between the hydrogel and glass/stainless steel.<sup>72,73</sup> Although PAETA-Ac/CNT in a wet state shows weakened adhesion strength, it can still withstand a load that is 1000 times its own weight (insets of Fig. S11d, ESI<sup>†</sup>). Due to the good adhesion performance, the PAETA-Ac/CNT hydrogel can adhere to the surface of a glass dish easily for outdoor AWH. The adhesion performance is also beneficial for air-conditioning applications by adhering hydrogels to the surface of a metal heat exchanger.





**Fig. 6** (a) Tailored PAETA-Ac/CNT hydrogels with triangle, square, and M shapes. The hydrogels (i) before cutting, (ii) after cutting, and (iii) after adhesion together by gentle contact. (b) Water uptake of PAETA-Ac/CNT hydrogel and the ambient conditions in the outdoor water vapor sorption experiment. Inset is a digital photo of the PAETA-Ac/CNT hydrogel attached to the glass dish. (c) Digital photo of the AWH system for the outdoor AWH test with the (1) AWH device, (2) thermocouple temperature transfer module, (3) thermohygrometer, (4) sensor of thermohygrometer, and (5) solar power meter. (d) Sunlight intensity variation and temperature changes of the hydrogel, container, and ambient air in the outdoor AWH experiment (water production step). (e) Digital photos of (i) the AWH device, (ii) condensed water at the bottom of the container, and (iii) collected water at the end of the outdoor water desorption process. (f) The quality of collected water from an outdoor AWH test.

During the outdoor water sorption process, PAETA-Ac/CNT hydrogel was exposed to ambient conditions to sorb water vapor between 7:00 pm on April 4, 2020 and 6:00 am on April 5, 2020 (KAUST campus, Thuwal, Saudi Arabia), whose weather conditions are shown in Fig. 6b. Then the hydrogel with ~15.1 g of the sorbed water was placed inside an enclosed device with a transparent plastic top wrap, which was then exposed to natural sunlight from 10:30 am to 2:00 pm on April 5, 2020 (Fig. 6c and Fig. S12, ESI<sup>†</sup>). Due to the excellent photothermal property of CNTs, the hydrogel layer was heated up to ~60 °C within the first 17 min before reaching a steady-state temperature of ~82 °C by ~150 min (Fig. 6d). At 2:00 pm, ~10.7 g water, with a rate of ~0.53 g g<sup>-1</sup>, was collected by the device (Fig. 6e). The quality of the collected water was analyzed, and the results show that the total organic carbon (TOC), total nitrogen (TN), Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> concentrations of the water were all lower than the WHO standard for drinking water (Fig. 6f).<sup>74</sup>

### 3. Conclusions

In summary, we have demonstrated the synthesis of PAETA-X hydrogels which are quaternary ammonium-based crosslinking polycations paired with benign-anions. PAETA-X hydrogels with the benign-anions not only provide improved water vapor sorption capacity but also have reduced corrosivity to metal. PAETA-X hydrogels are crosslinked, possess chemical and physical stability, and have solid state when wet. PAETA-X hydrogels are versatile vapor sorbents working in a wide range of relative humidities.

PAETA-Ac produces a COP<sub>C</sub> of 0.75 with a temperature lift of 20 °C at a low regeneration temperature of 70 °C during an air-conditioning process. PAETA-Ac also produces ~0.53 g g<sup>-1</sup> fresh water in an outdoor field AWH test from one cycle. The synthesis method of halide-free PAETA-X developed in this work provides a new route for the fabrication of better water vapor sorbents for significant applications at the water-energy nexus.

## 4. Experimental section

### Materials

[2-(Acryloyloxy)ethyl]trimethylammonium chloride solution (AETA-Cl; 80 wt% in water), ammonium persulfate (APS), *N,N'*-methylenebisacrylamide (BIS), *N,N,N',N'*-tetramethylethylenediamine (TEMED), sodium chloride (NaCl), sodium acetate (NaAc), sodium oxalate (Na<sub>2</sub>Ox), and sodium citrate dihydrate (Na<sub>3</sub>Cit) were purchased from Sigma-Aldrich. Deionized water (18.2 MΩ cm) was used for all experiments. All chemicals were used as received without further purification.

### Fabrication of PAETA-X hydrogels

The PAETA-Cl hydrogel was fabricated by free radical polymerization of AETA-Cl monomer, which was initiated by APS in the presence of BIS as the crosslinking agent. Briefly, 2 mg of BIS, and 10 mg of APS were added into 2 mL of 50 wt% AETA-Cl aqueous solution. Then, the mixed solution was treated by ultrasonication in an ice-water bath for 5 min and then treated with nitrogen for 10 min to remove the oxygen in the solution.



Finally, 10  $\mu\text{L}$  of TEMED was added, and then the mixed solution was sealed and kept at room temperature for 12 h to polymerize into the original PAETA-Cl hydrogel.

The purified PAETA-Cl hydrogel and PAETA-X hydrogels paired with other counter anions ( $\text{Ac}^-$ ,  $\text{Ox}^{2-}$  and  $\text{Cit}^{3-}$ ) were prepared *via* the ion-exchange method. Briefly, the original PAETA-Cl hydrogel was immersed in an aqueous solution of 5 wt% NaCl, 5 wt% NaAc, 3 wt%  $\text{Na}_2\text{Ox}$ , and 5 wt%  $\text{Na}_3\text{Cit}$  for 12 h 3 times followed by immersion in water for 12 h 6 times, respectively. The hydrogel was finally dried at 80  $^\circ\text{C}$  in an oven to obtain purified PAETA-X, with X being  $\text{Cl}^-$ ,  $\text{Ac}^-$ ,  $\text{Ox}^{2-}$  or  $\text{Cit}^{3-}$ .

### Material characterization

ATR-FTIR spectra of PAETA-X were obtained on a Nicolet iS10 FTIR spectrometer by using the Thermo Scientific Smart iTX ATR sampling accessory. Energy dispersive spectroscopy (EDS) spectra were performed using an EDAX EDS detector attached to an FEI Quanta 600 SEM. PAETA-X hydrogels were placed in contact with aluminum plates for 60 days to assess their corrosivity by an optical microscope (Nikon AZ100M). The thermal stability of the hydrogels was determined by a thermogravimetric analyzer (TGA, NETZSCH TG 209 F1 Iris<sup>®</sup>) with the heating rate of 10  $^\circ\text{C min}^{-1}$  under a nitrogen atmosphere. The glass transition temperature ( $T_g$ ) and specific heat capacity ( $c_p$ ) of PAETA-X were determined using a differential scanning calorimeter (DSC, TA Discovery DSC 250) under the modulation mode with the temperature range from  $-80$  to  $120$   $^\circ\text{C}$  at a heating rate of 2  $^\circ\text{C min}^{-1}$  in a nitrogen atmosphere. Water vapor sorption/desorption isotherms were measured by an intelligent gravimetric analyzer (IGA, Hiden Isochema IGAsorp-CT). Static water vapor sorption-desorption curves and multiple cycles of water sorption-desorption were performed on a simultaneous thermal analyzer (STA, NETZSCH STA 449 F3 Jupiter<sup>®</sup>) connected with a modular humidity generator (ProUmid GmbH & Co. KG, MHG32). The humidity was controlled by a humidified nitrogen gas flow, which was passed through the thermogravimetric balance. It is worth mentioning that the water vapor was produced at room temperature ( $\sim 21$   $^\circ\text{C}$ ), which was lower than the temperature of thermogravimetric balance in our tests. The adhesion performance of PAETA-Ac/CNT hydrogel was determined through lap shear tests using a Universal Testing Machine (Instron 5944). A hydrogel ( $20 \times 26 \times 1$   $\text{mm}^3$ ) was sandwiched between two glass slides or two stainless steel sheets. All tests were performed at a tensile speed of  $60$   $\text{mm min}^{-1}$  at room temperature.

In conducting the outdoor AWH experiment, a simple and homemade all-in-one device was used. For the outdoor test, 2.5 wt% CNT<sup>15</sup> (mass ratio of CNT and AETA-Cl monomer) was added in the synthesis process of PAETA-Cl, and PAETA-Ac/CNT hydrogel was obtained following otherwise the same procedure. A thermocouple temperature transfer module (SULINKIOT RS20K-C) with two 0.5 mm K-type thermocouple sensors was used to monitor the temperature changes of the hydrogel and condenser. A thermohygrometer (SULINKIOT CX03) was used to record the RH and temperature of ambient air, and a solar power meter (TES-1333R) was used to record the sunlight

intensity. The ion concentrations of the collected water were detected using the inductively coupled plasma-optical emission spectrometry instrument (ICP-OES, Agilent 5110). The total organic carbon (TOC) and total nitrogen (TN) were detected using a total organic carbon analyzer (TOC-L, SHIMADZU).

### Conflicts of interest

There are no conflicts to declare.

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