Supplementary Information

Metal- and Halide-Free, Solid-State Polymeric Water Vapor Sorbents for Efficient Water-Sorption-Driven Cooling and Atmospheric Water Harvesting

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Fig. S1 Digital photos of (a) aqueous solution of 50% wt AETA-Cl monomer, (b) solid PAETA-Cl hydrogel (i) in a glass vial and (ii) taken out of the glass vial, and (c) small pieces of PAETA-Cl hydrogel, directly cut from the same hydrogel in (b).



Fig. S2 ATR-FTIR spectrum of PAETA-Cit hydrogel in the 1450–1300 cm⁻¹ wavenumber range.



Fig. S3 Water sorption isotherms of PAETA-Cl and PAETA-Ac at 25 °C. Blue stars represent the inherent water sorption capacity at 80% RH or 100% RH of the hygroscopic polymers reported in the literatures. The inherent water vapor sorption capacity is the capacity of the pure polymers without modification.¹⁻⁸ The green stars represent the water sorption capacity of zeolite and silica gel.^{1,9}

Supplementary Note 1. Calculation of the enthalpy of sorption.^{10,11}

Enthalpy of sorption ($\Delta_s H$) for water can be calculated from two or more water vapor sorption isotherms at different temperatures:

$$\Delta_s H = -R \frac{T_1 T_2}{T_2 - T_1} \ln \frac{P_2}{P_1}$$
 Equation S1.

Here, T_1 (K) and T_2 are the temperatures for two sorption isotherms. P_1 (Pa) and P_2 are the absolute pressures at T_1 and T_2 , respectively, for a given water uptake.



Fig. S4 The binding energy of Cl⁻ and Ac⁻ with water molecules.

Anion	Cl	Ac	Ox ²⁻	Cit ³⁻
Formula	Cl	$C_2H_3O_2$	C_2O_4	$C_6H_5O_7$
Structure		~		
Surface Area (Å ²)	36.46	80.50	92.87	171.23

Table S1 Summary of the size information of various anions by using the Connolly surface.





Fig. S5 Principle of operation of a sorption-driven heat transformation cycle with the sorption stage (left) and the desorption stage (right).¹⁰

Supplementary Note 2. Calculation of the characteristic curve.¹⁰

In order to make the water uptake dependent on only one parameter (A, energy) rather than two parameters (P, T), the characteristic curve was adopted. A is Polanyi sorption potential, which is the molar Gibbs free energy of sorption with opposite sign:

$$A = RT \ln\left(\frac{P_0(T)}{P}\right)$$
 Equation S2.

Here, R (J K⁻¹ mol⁻¹) is the gas constant, T is temperature, P_0 is the temperature-dependent saturation vapor pressure of water, and P is the pressure at each water uptake.



Fig. S6 Water uptake as a function of absolute pressure at different temperatures for (a) PAETA-Cl, (b) PAETA-Ac, (c) PAETA-Ox, and (d) PAETA-Cit hydrogels.

Supplementary Note 3. Isosteric cycle diagram of a sorption-driven air conditioning cycle.^{10,12}

The sorption-driven air conditioning cycle can be briefly described through the isosteric cycle diagram, which consists of four steps (Fig. S7). In the step of I-II (isosteric heating), the sorbent is fully saturated with working fluid (water, W_{max}). Before the water can be released to the condenser, firstly, the pressure needs to be increased from evaporation pressure (p_{ev}) to condensation pressure (p_{con}) by heating the sorbent from T_1 to T_2 . In general, T_1 is chosen to be equal to the condenser temperature (T_{con}). In this step, the sorbent vessel is disconnected with the evaporator and

condenser, and no sorbed water is desorbed. In the step of II-III (isobaric desorption), the sorbent vessel is connected to the condenser, and the sorbed water is allowed to desorb by continuous heating the sorbent from T_2 to desorption temperature (T_{des}) with constant pressure. When the T_{des} is reached, the water uptake reaches its minimum value (W_{min}). The desorbed water ($W_{max} - W_{min}$) is condensed in the condenser, releasing heat to the ambient environment (Q_{con}). The energy input for the steps of I-II (Q_{I-II}) and II-III (Q_{II-III}) is the energy required for desorption, which is the energy for regeneration of sorbent (Q_{regen}).



Fig. S7 Isosteric cycle diagram for a sorption-driven heat pump cycle. For practical applications, in most cases T_1 is chosen to equate to T_{con} .^{10,12}

In the step of III-IV (isosteric cooling), the sorbent has been regenerated and is able to be used for sorption process. The sorbent vessel is again disconnected from the evaporator and condenser, and the pressure is needed to be reduced from p_{con} to p_{ev} by cooling the sorbent from T_{des} to T_3 . In this step, ideally, no water vapor is sorbed. In the step of IV-I (isobaric sorption), the sorbent vessel is connected to the evaporator, and the sorbent is allowed to sorb the water vapor with continual cooling under constant pressure. When T_1 is reached, the water uptake reaches its maximal value again (W_{max}). The energy released during the steps of III-IV (Q_{III-IV}) and IV-I (Q_{IV-I}) is equal to the energy for sorption (Q_s).

For cooling purpose, the sorbed water $(W_{\text{max}} - W_{\text{min}})$ takes up energy from the ambient environment in the evaporator by its evaporation (Q_{ev}) . This process occurs at a low temperature which is below the ambient temperature, where the achievable decrease in temperature is used for

cooling. The energy input for the steps of I-II and II-III is used for the regeneration of sorbent (Q_{regen}) .

Supplementary Note 4. Thermodynamic calculations of a sorption-driven air conditioning cycle.¹⁰⁻¹²

The coefficient of performance for cooling (COP_C) is commonly used to describe the energy efficiency of a sorption-driven air conditioning cycle from a thermodynamic perspective. The COP_C value is defined as the useful cooling energy output divided by the energy required as input:

$$COP_{c} = \frac{Q_{ev}}{Q_{regen}}$$
 Equation S3.

Here, $Q_{ev}(kJ)$ is the energy taken up by the evaporator, and can be calculated with the enthalpy of evaporation $\Delta_{vap}H(kJ/mol)$ at T_{ev} :

$$Q_{ev} = \frac{\Delta_{vap} H(T_{ev}) m_{sorbent} \Delta W}{M_w}$$
Equation S4.

Here, m_{sorbent} is the amount of sorbent and is omitted here, and thus Q is defined as the energy value per unit mass of the sorbent. ΔW (g g⁻¹) is the working capacity, defined as the mass difference between the maximal and minimum loadings of working fluid (W_{max}-W_{min}). M_w (g mol⁻¹) is the molar mass of working fluid, and water is the working fluid in this work. The energy required for regeneration of sorbent (Q_{regen}) consists of the energy input for the steps of isosteric heating (I-II, Q_{I-II}) and isobaric desorption (II-III, Q_{II-III}): $Q_{regen} = Q_{I-II} + Q_{II-III}$ Equation S5.

The energy input for isosteric heating (I-II, Q_{I-II}) can be calculated with:

$$Q_{1-1I} = \int_{T_{con}}^{T_2} c_p^{eff}(T) dT + \int_{T_{con}}^{T_2} W_{max} c_p^{wf}(T) dT$$
Equation S6.

Here, c_p^{eff} (J g⁻¹·K⁻¹) is the effective heat capacity of sorbent and heat exchanger. In order to compare the intrinsic properties of sorbents, the mass of heat exchanger is assumed to be zero in the calculation, thus the c_p^{eff} value is equal to the heat capacity of sorbent ($c_p^{sorbent}$). c_p^{wf} is the heat capacity of working fluid.

The energy input for isobaric desorption (II-III, Q_{II-III}) can be calculated with:

$$Q_{\text{II-III}} = \int_{T_2}^{T_{des}} c_p^{eff}(T) \, dT + \int_{T_2}^{T_{des}} \frac{W_{max} + W_{min}}{2} c_p^{wf}(T) \, dT - Q_{sorption}$$

Equation S7.

Here, Q_{sorption} is the energy released during the sorption of working fluid and can be calculated with:

$$Q_{sorption} = \frac{1}{M_w} \int_{W_{min}}^{W_{max}} \Delta_s H(W) \, dW$$
 Equation S8.

According to the above Equations, the COP_C value can be determined.



Fig. S8 Specific heat capacity as a function of temperature for PAETA-X hydrogels.



Fig. S9 Water vapor sorption-desorption cycles for (a) PAETA-Cl, (b) PAETA-Ac, (c) PAETA-Ox, and (d) PAETA-Cit hydrogels. The sorption process was performed at 30 °C in a nitrogen flow with RH of 70%, and the desorption process was carried out at 70 °C in a nitrogen flow with RH of 10%.



Fig. S10 Corrosion assessment of PAETA-X hydrogels on aluminum plates. Digital photos of (a) original aluminum plates, (b) PAETA-X hydrogels on aluminum plates (i. PAETA-Cl, ii. PAETA-Ac, iii. PAETA-Ox, and iv. PAETA-Cit), (c) the aluminum plates after 60 days of contact with PAETA-X hydrogels. (d) Microscope images of the selected areas in (c).



Fig. S11 The adhesion strength of PAETA-Ac/CNT hydrogel with the glass slides (a, c) and stainless steel sheets (b, d). The wet hydrogel contains 1 g g^{-1} of water. The insets of (d) are the photos of PAETA-Ac/CNT hydrogel sticks between a glass slide and a stainless steel weight.



Fig. S12 Digital photos of PAETA-Ac hydrogel-based AWH device after (a, b) 30 s and (c) 3.5 h of exposure to the sunlight. The arrows in (a) represent the thermocouple sensor inside the hydrogel layer and outside the container wall, respectively.

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