## Molecular Machine Acts as Waterwheel in Artificial Water Channel and Isotope Effect on Water Adsorption Kinetics

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We report a compound with the formula of  $(4-ApyH^+)(DB[24]crown-8)[Ni(dmit)_2]^-(H_2O)$ (1•H<sub>2</sub>O) (where 4-ApyH<sup>+</sup> is 4-aminopyridinium<sup>+</sup>, DB[24]crown-8 is dibenzo[24]crown-8, and dmit<sup>2-</sup> is 2-thioxo-1,3-dithiole-4,5-dithiolate). Crystal 1•H<sub>2</sub>O keeps the single crystallinity after losing 0.7 molecule of water per unit by heating at 100 °C for 2 h, affording 1.0.3H<sub>2</sub>O. When exposing 1.0.3H<sub>2</sub>O in air for 12 h, 1.H<sub>2</sub>O is recovered. In the reversible H<sub>2</sub>O ad/desorption process, the overall structural framework remains unchanged except for disorders in H<sub>2</sub>O position, 4-ApyH<sup>+</sup> rotation and DB[24]crown-8 deformation (Fig 1). In 1•H<sub>2</sub>O, both H<sub>2</sub>O and DB[24]crown-8 are ordered and the two configurations of DB[24]crown-8 (vellow and green) are hydrogen-bonded with H<sub>2</sub>O and with amino groups of 4-ApyH<sup>+</sup>, respectively. While in 1.0.3H<sub>2</sub>O, 4-ApyH<sup>+</sup> cations are disordered over two sites with each 50% occupancy (blue and magenta). Meanwhile, the remaining 0.3 molecule of H<sub>2</sub>O are also disordered in two positions and DB[24]crown-8 becomes identical and takes similar conformation with that of green one in 1•H<sub>2</sub>O. The possible H<sub>2</sub>O adsorption mechanism can be regarded as a series of waterwheels at the molecular size. During the desorption process, with the loss of H<sub>2</sub>O, crystalline space for molecular rotation is generated, allowing in-plane molecular rotation of 4-ApyH<sup>+</sup>. As a result, 4-ApyH<sup>+</sup> molecules invert 180 degree and flexible DB[24]crown-8 columns shrink. Upon the rehydration process, a H<sub>2</sub>O molecule coordinated to a pyridinium N<sup>+</sup> site through N-H<sup>+</sup>•••O hydrogen bond. With the 4-ApyH<sup>+</sup> rotation, the H<sub>2</sub>O molecules move to the next position, which can form hydrogen bond with the next 4-ApyH<sup>+</sup>. The rotation of 4-ApyH<sup>+</sup> is possible given that H<sub>2</sub>O molecules are not occupied at the next site. Finally, one of the DB[24]crown-8 expand from green to yellow

conformation and 1•H<sub>2</sub>O with fully occupied with H<sub>2</sub>O molecule at yellow DB[24]crown-8 has ordered structure. This step-by-step structural transformation in the adsorption process is in good agreement with the H<sub>2</sub>O adsorption isotherm at 298 K. Kinetic adsorption measurements show great isotopic effect in H<sub>2</sub>O /D<sub>2</sub>O adsorption rates. The stronger antiferromagnetic interaction in 1•0.3H<sub>2</sub>O corresponds to closer molecular contacts due to slight shrinkage of the supramolecular column upon desorption of H<sub>2</sub>O molecule.



Fig. 1. Supramolecular cation structures in the reversible H<sub>2</sub>O ad/desorption process.