

Figure SI. Electron density isorfaces of the $H_2VO_4^-/pyrrole$ complex as obtained from HCTH/PW calculations. Red and blue surfaces enclose the 90% and 95% of the total electron density, respectively. The VO_2^+ is clearly visible in the equatorial plane of the complex.

Supplementary Information

To investigate the chemical nature of vanadate moiety, we calculated Mayer's bond orders, B, which give insights regarding the relative strength of ionic and covalent bonding between a given pair of atoms. We recall that, for an appropriate choice of basis set, a vanishing bond order between an atom pair would indicate either no bonding or a perfectly ionic bond, a value of one, two and so on would correspond to a single, double, etc. covalent bond. Fractional values would then be interpreted as a mixture of ionic and covalent bonding bonding. The V–OH interaction is predominatly ionic ($B_{\rm V-OH} = 0.24$), whereas the V–O bond is covalent with some partial double bond character ($B_{\rm V-O} = 1.07$). The direct analysis of electron density (Fig. SI) supports this conclusion. Therefore, the vanadate moiety in its di-protonated form may be more likely ascribed to a dioxovanadium(V) species (VO₂⁺), which strongly interacts with OH⁻ anions.