

**Two New Molybdates Based on $\infty[\text{Mo}_n\text{O}_{3n+1}]^{2-}$ Units (n = 11, 4)
with Proton Conduction under Ionothermal**

Y. H. Zhao,^a X. C. Jin,^a L. Chen,^a Y. F. Ding,^a Z. Mao,^a H. Fu^{*a,b} and Y. H. Ao^{*a,b}

^a School of Chemistry and Life Science, and Advanced Institute of Materials Science, Changchun University of Technology, Changchun, Jilin, P. R. China. Email: Mr.fuhai@163.com

^b School of Chemistry and Life Science, Jilin Province Key Laboratory of Carbon Fiber Development and Application Changchun University of Technology Changchun, Jilin, P. R. China. Email: aoyuhui@mail.ccut.edu.cn

Table of contents

- 1. General experimental information**
- 2. Supplementary structural figures of compound 1 and 2**
- 3. TGA and DTA figures of compound 1 and 2**
- 4. References**

1. General experimental information

1.1 preparation of [Emim]Br (1-ethyl-3-methylimidazolium bromide)

Ethyl bromide (6.5 g, 60 mmol) and N-methylimidazole (4.9 g, 60 mmol) was added into a flask equipped with a condenser and magnetic stirrer. The flask was placed in a silicone oil bath and the bath was heated to 140 °C during a 10 minute period. During the latter stages of heating, an exothermic reaction took place forming an emulsion that disappeared after a few minutes to afford a transparent, golden, slightly viscous solution. When the emulsion disappeared, the flask was removed from the oil bath and the contents were allowed to stir and cool for 10 minutes. The flask was placed into the oil bath at 140 °C for another 10-15 minutes. The contents were dried under vacuum at 100-120 °C to produce the 1-ethyl-3-methylimidazolium bromide.

1.2 preparation of Bis-(4-imidazol-1-yl-phenyl)-diazene¹

(i) Preparation of 1-(4-Nitrophenyl)-1H-imidazole.

A mixture of imidazole (2.1 g, 31.18 mmol) and anhydrous K₂CO₃ (5.8 g, 42.52 mmol) in DMF was heated for 30 min with vigorous stirring. After that, 4-fluoronitrobenzene (4 g, 28.34 mmol) was added over a period of 15 min. The mixture was refluxed for 24 h, cooled to RT, and then added to ice-water. On standing, a yellow-colored precipitate was formed which was collected by filtration, washed with ice-cold water, and dried in air to get the pure compound.

(ii) Preparation of Bis-(4-imidazol-1-yl-phenyl)-diazene

A suspension of 1-(4-nitrophenyl)-1H-imidazole (5 g, 26.45 mmol) in 2-propanol was heated to reflux to obtain a clear solution. Then aq NaOH (12 g in 30 mL H₂O) and Zn powder (30 g) were added to the mixture. It was then refluxed for 24 h and allowed to cool to RT, and all insoluble materials present were removed by filtration. Upon removal of the solvent under reduced pressure, the product was extracted with chloroform. The organic layer was washed several times with water, dried over anhydrous Na₂SO₄, and finally evaporated under reduced pressure to obtain a bright-orange solid which was recrystallized from hexane/chloroform to get the pure compound

2. Supplementary structural figures of 1 and 2

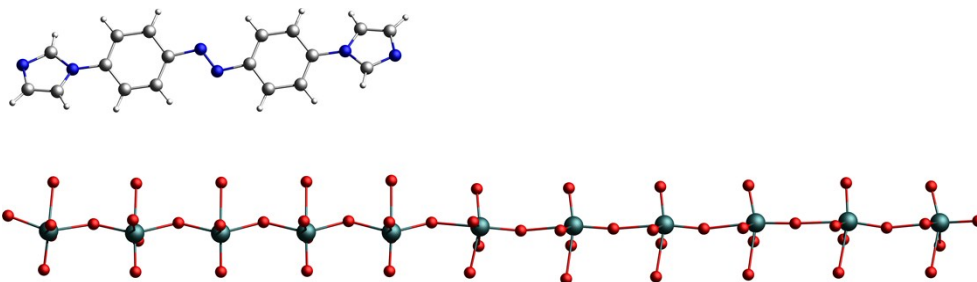


Fig. S1 the ball and stick representations of unit cell in **1**, Mo atoms dark green balls, O atoms red balls, N atoms dark blue balls, C atoms gray balls.

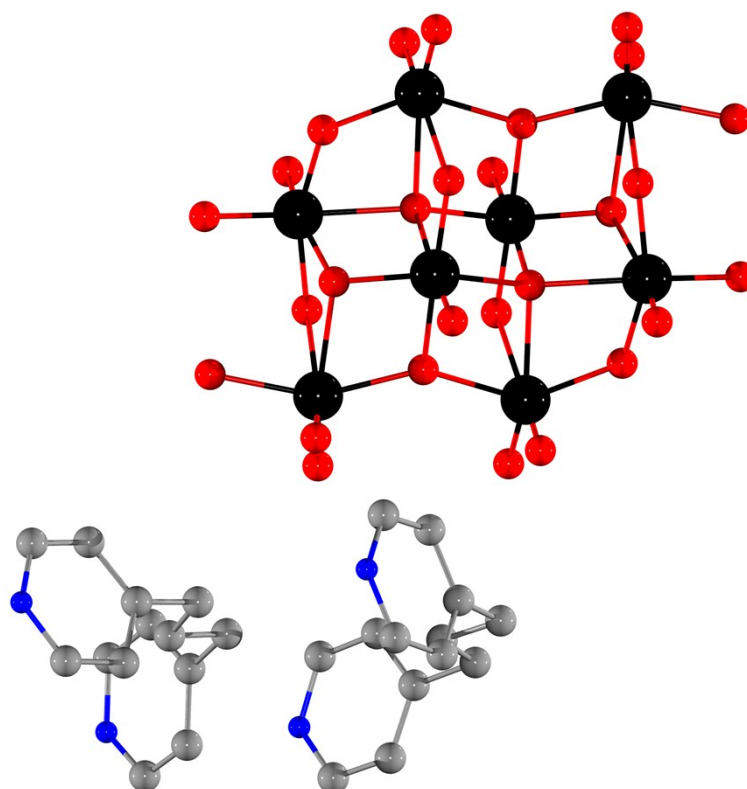


Fig. S2 the ball and stick representations of the unit cell of **2**, Mo atoms black balls, O atoms red balls, N atoms dark blue balls, C atoms gray balls.

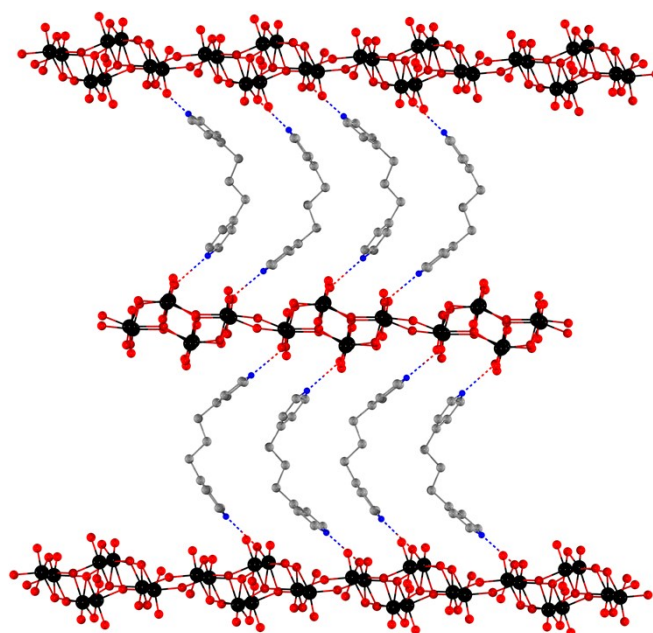


Fig. S3 the ball and stick representations of H-bonds in **2**, Mo atoms black balls, O atoms red balls, N atoms dark blue balls, C atoms gray balls, H-bonds two colour dotted lines.

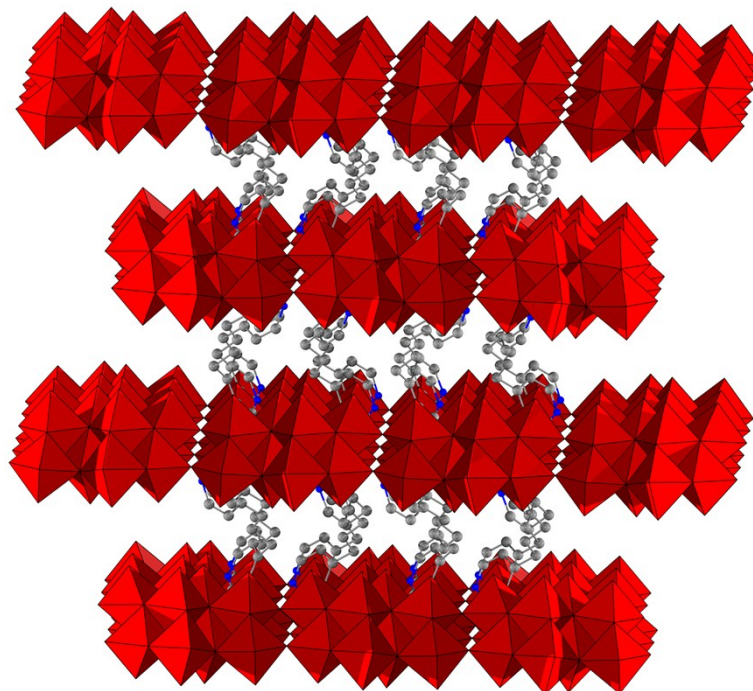


Fig. S4 the ball-stick and polyhedron representations of 3D supermolecule stacking in **2**, N atoms dark blue balls, C atoms gray balls.

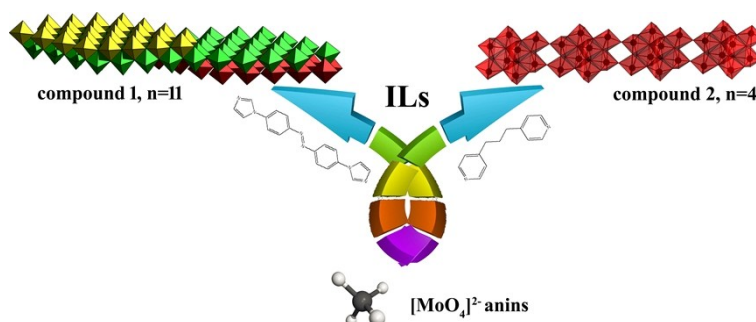


Fig. S5 two different kind of organic ligands were introducing into the reaction system (ILS) towards the $\infty[\text{Mo}_n\text{O}_{3n+1}]^{2-}$ blocks, resulted two different n value ($n = 11, 4$).

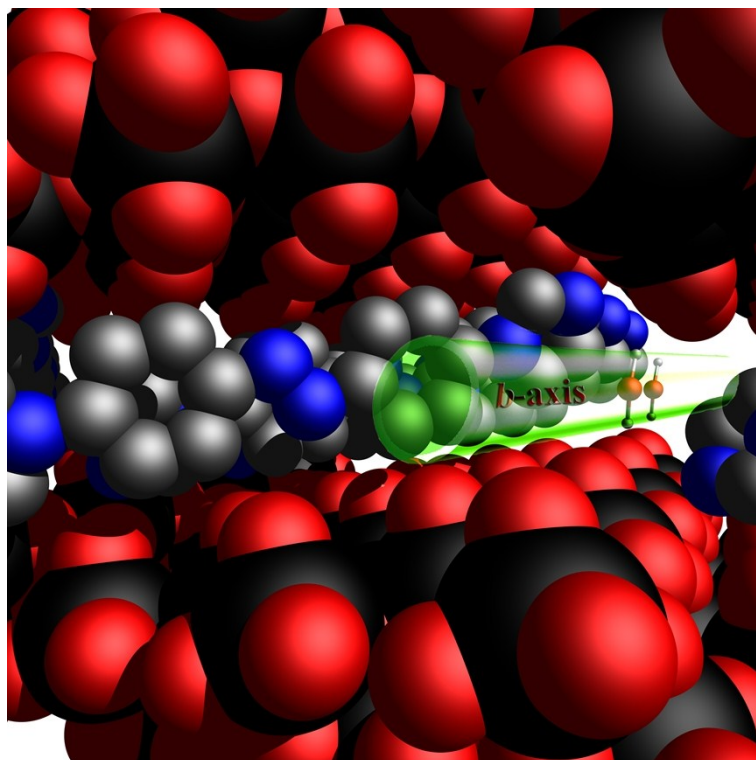


Fig. S6 the schematic diagram of proton conductivity of **1**.

3. TGA and DTA figures of **1** and **2**

9.8 mg dry crystals of **1** were weighed at the room temperature, and DSC/TGA were measured by flowing dry nitrogen with a heating and cooling rate of $20\text{ }^{\circ}\text{C min}^{-1}$ on a TA TGAQ500 between 40 and $800\text{ }^{\circ}\text{C}$. The thermogravimetric analysis (TGA) of **1** (Fig. S7, ESI†) reveals a weight loss of nearly 1% from $150\text{ }^{\circ}\text{C}$ to $300\text{ }^{\circ}\text{C}$, which corresponds to the crystal water, a weight loss of about 17% from $320\text{ }^{\circ}\text{C}$ to $450\text{ }^{\circ}\text{C}$, which corresponds to the organic ligand L1. The third mass loss begins at $600\text{ }^{\circ}\text{C}$, and is associated with the decomposition of $^{2}/_{\infty}[\text{Mo}_{11}\text{O}_{34}]^{2-}$ anions.

The DTA of **1** is recorded simultaneously with TGA curves. The DTA curve shows first order transition namely crystallization. After losing the crystal water, the compound may undergo decomposition reactions at higher temperature which give broad peaks; these may be generally exothermic but are sometimes more complex in nature.

6.8 mg dry crystals of **2** were weighed at the room temperature, and DSC/TGA were measured by flowing dry nitrogen with a heating and cooling rate of 20 °C min⁻¹ on a TA TGAQ500 between 40 and 800 °C. The thermogravimetric analysis (TGA) of **2** (Fig. S8, ESI†) reveals a weight loss of about 28% from 230 °C to 290 °C, which corresponds to the organic ligand L2. The second mass loss begins at 350 °C, and is associated with the decomposition of $1/\infty[\text{Mo}_4\text{O}_{13}]^{2-}$ anions.

The DTA of **2** is recorded simultaneously with TGA curves. The DTA curve shows two decomposition reactions at higher temperature which give broad peaks; these may be generally exothermic but are sometimes more complex in nature.

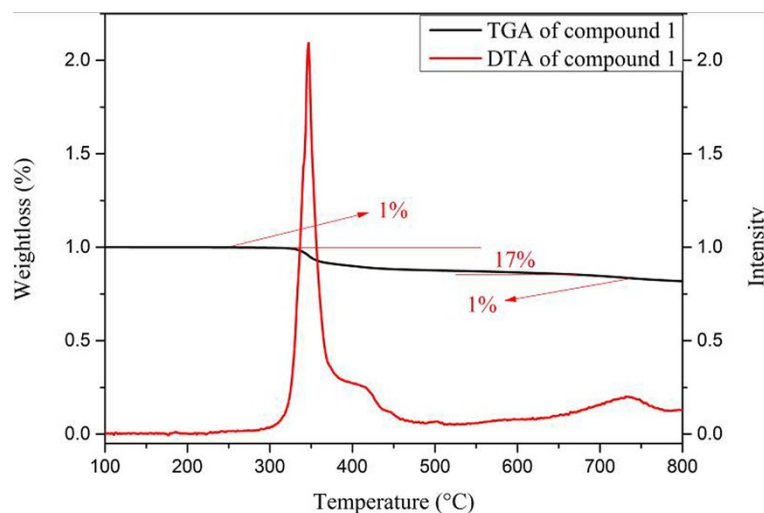


Fig. S7 thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of **1**.

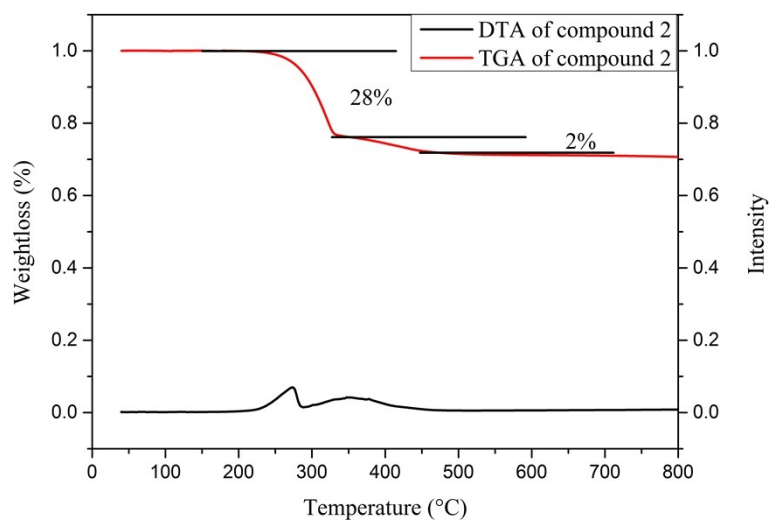


Fig. S8 thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of **2**.

4. Reference

- 1 K. S. Manish and K. B. Parimal Inorg., Chem. 2011, 50, 1889-1897