

## Supporting Information

### Pristine Organo-imido Polyoxometalates as an Anode for Lithium Ion Batteries

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#### Materials and Methods:

During the course of reactions, octamolybdate has been synthesized according to the literature<sup>S1,S2</sup> to further react with our synthesized ligand amine. 2,6-dimethyl aniline has been purchased by TCI while all other solvents used as purchased except MeCN that was dried by refluxing over CaH<sub>2</sub> prior to use in reaction. The IR has been done at Perkin Elmers Infrared spectrometer, using KBr pellet method. UV-Vis spectroscopy has been done at UV2100S spectrophotometer using the solutions in MeCN. ESI-MS has been done at ion trap mass spectrometry machine (Thermofisher LTQ). Likewise, <sup>1</sup>H-NMR data has been collected at JASTEC JEOL 400 Hz NMR spectrophotometer. Single crystal data collection has been done at Oxford Gemini Diffractometer and refined via using SHELXTL<sup>S3</sup> and OLEX2<sup>S4</sup> programs. Elemental analysis has been done at Thermo-Quest Flash EA 1112-Series analyzer.

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<sup>S1</sup> L. Xu, M. Lu, B. Xu, Y. Wei, Z. Peng, D. R. Powell, *Angew. Chem. Int. Ed.*, 2002, **41**, 4129.

<sup>S2</sup> T.-C. Hsieh, S. N. Shaikh, J. Zubietta, *Inorg. Chem.*, 1987, **26**, 4079.

<sup>S3</sup> G. M. Sheldrick, SHELXTL v. 5.10, *Structure Determination Software Suite*, Bruker AXS, Madison, Wisconsin (USA), 1998.

<sup>S4</sup> O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program *J. Appl. Cryst.*, 2009, **42**, 339.

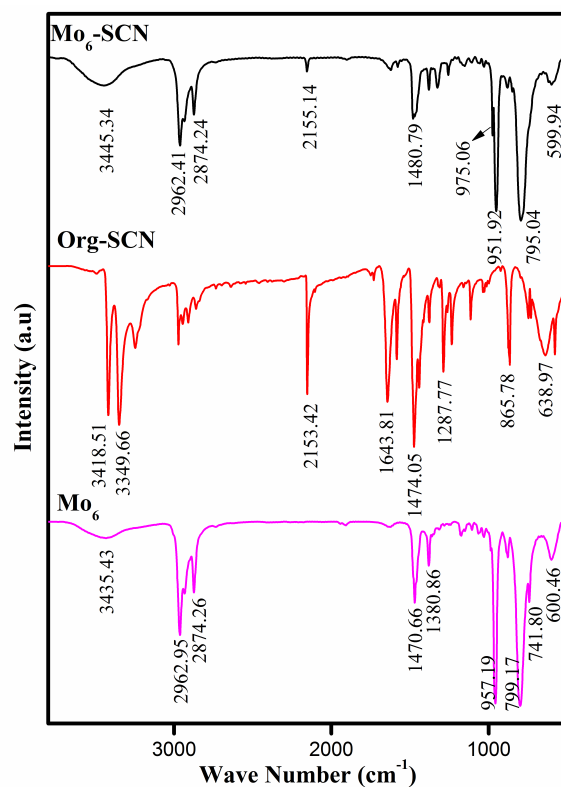


Figure S1. IR spectra for the new hybrid (Mo<sub>6</sub>-SCN), ligand (Org-SCN) and POM (Mo<sub>6</sub>), peaks around 952 and 796 cm<sup>-1</sup> that can easily be assigned to the stretching vibrations of Mo-O<sub>t</sub> and Mo-O<sub>b</sub>-Mo groups respectively, while characteristic peaks at about 975 and 2155 cm<sup>-1</sup> belong to Mo≡N and C≡N (from -SCN group) respectively.

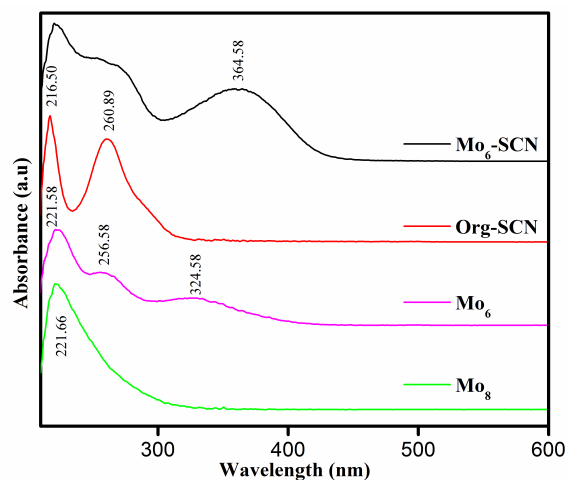


Figure S2. UV-VIS spectra for the new hybrid POM ( $\text{Mo}_6\text{-SCN}$ ), ligand ( $\text{Org-SCN}$ ) and POMs ( $\text{Mo}_6$  and  $\text{Mo}_8$ ), data shows significant bathochromic shift, due to  $d\text{-}\pi$  interactions, from nearly 325 nm for hexamolybdate to about 365 nm for hybrid compound  $\text{Mo}_6\text{-SCN}$ .

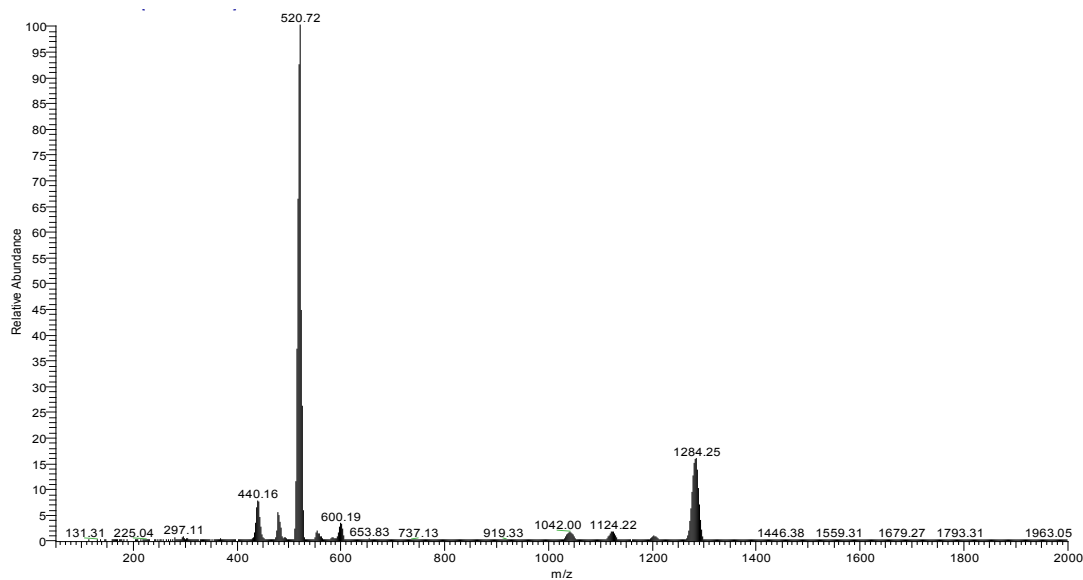


Figure S3. ESI-MS spectra for  $\text{Mo}_6\text{-SCN}$ , shows clearly resolved peaks at  $m/z$  about 520 for  $[\text{Mo}_6\text{O}_{18}(\text{N-Ph-(Me)}_2\text{-SCN})]^{2-}$ , and at  $m/z$  about 1284 for  $(\text{Bu}_4\text{N})[\text{Mo}_6\text{O}_{18}(\text{N-Ph-(Me)}_2\text{-SCN})]^-$ .

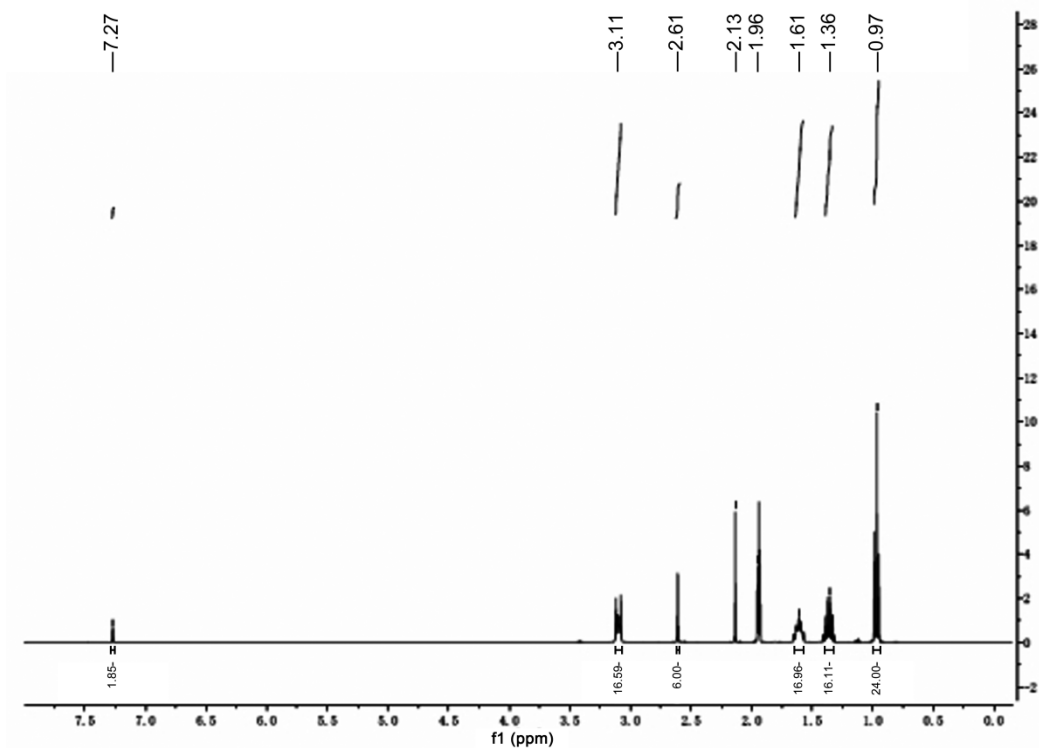


Figure S4. <sup>1</sup>H NMR spectra for Mo<sub>6</sub>-SCN (Peaks at 1.94 and 2.13 belong to solvent (acetonitrile) and water content respectively), the triplets at 0.97 and 3.11 ppm, while sextet and pentet at 1.36 and 1.61 respectively can easily be assigned to Bu<sub>4</sub>N cation, while the singlet shifts at 2.61 and 7.27 are assigned to methyl groups hydrogen and phenyl ring hydrogen respectively.

Table S1. Single crystal X-ray crystallographic datafor Mo<sub>6</sub>-SCN

| Compound                                        | <b>Mo<sub>6</sub>-SCN (needle shaped crystal)</b>                                |
|-------------------------------------------------|----------------------------------------------------------------------------------|
| Empirical formula                               | C <sub>41</sub> H <sub>82</sub> Mo <sub>6</sub> N <sub>4</sub> O <sub>19</sub> S |
| Size [mm <sup>3</sup> ]                         | 0.40×0.12×0.10                                                                   |
| Temperature [K]                                 | 103                                                                              |
| Formula weight                                  | 1542.81                                                                          |
| Crystal system                                  | triclinic                                                                        |
| Space group                                     | <i>P</i> $\bar{1}$                                                               |
| <i>a</i> [Å]                                    | 12.6748(17)                                                                      |
| <i>b</i> [Å]                                    | 12.7588(8)                                                                       |
| <i>c</i> [Å]                                    | 19.564(3)                                                                        |
| $\alpha$ [°]                                    | 72.332(10)                                                                       |
| $\beta$ [°]                                     | 72.079(3)                                                                        |
| $\gamma$ [°]                                    | 78.863(8)                                                                        |
| <i>V</i> [Å <sup>3</sup> ]                      | 2850.9(6)                                                                        |
| <i>Z</i>                                        | 2                                                                                |
| <i>D</i> calc. [g/cm <sup>3</sup> ]             | 1.797                                                                            |
| Absorption coeff. [mm <sup>-1</sup> ]           | 1.386                                                                            |
| <i>F</i> (000)                                  | 1552                                                                             |
| $\theta$ range [°]                              | 3.25 to 26.0                                                                     |
| Reflections collected                           | 27954                                                                            |
| <i>R</i> (int)                                  | 0.0365                                                                           |
| GOF on <i>F</i> <sup>2</sup>                    | 1.154                                                                            |
| Final R indices [ <i>I</i> >2sigma( <i>I</i> )] | <i>R</i> <sub>1</sub> = 0.0583, <i>wR</i> <sub>2</sub> = 0.1087                  |
| R indices (all data)                            | <i>R</i> <sub>1</sub> = 0.0748, <i>wR</i> <sub>2</sub> = 0.1163                  |
| Largest diff. peak and hole                     | 1.16 and -1.35e.Å <sup>-3</sup>                                                  |

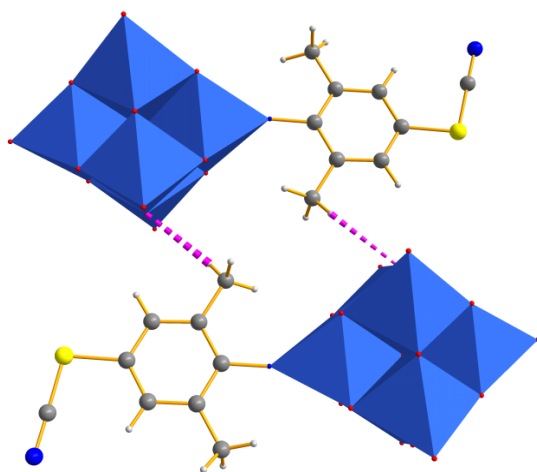


Figure S5. Dimeric form of Mo<sub>6</sub>-SCN, existing in crystal lattice due to H-bonding.

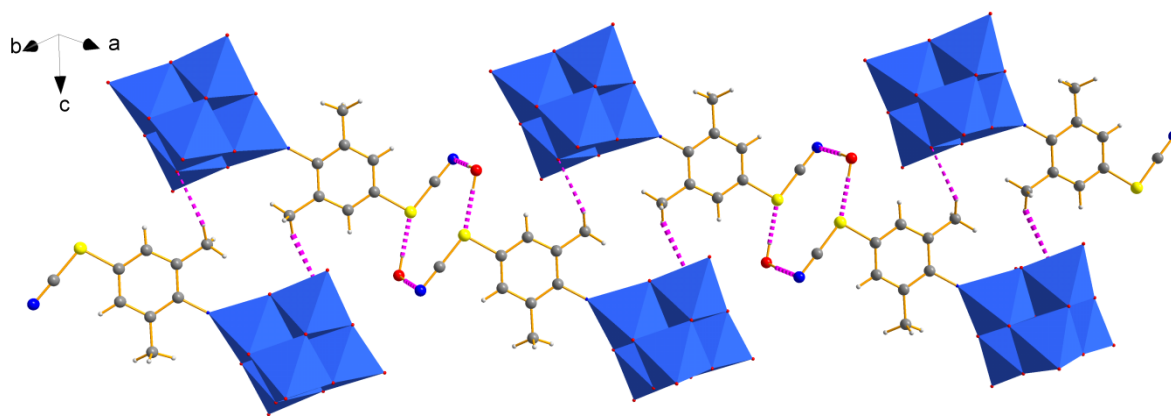


Figure S6. A view of crystal lattice of Mo<sub>6</sub>-SCN depicting the 1D chain supramolecular structure formed due to the hydrogen bonding between water and Mo<sub>6</sub>-SCN.

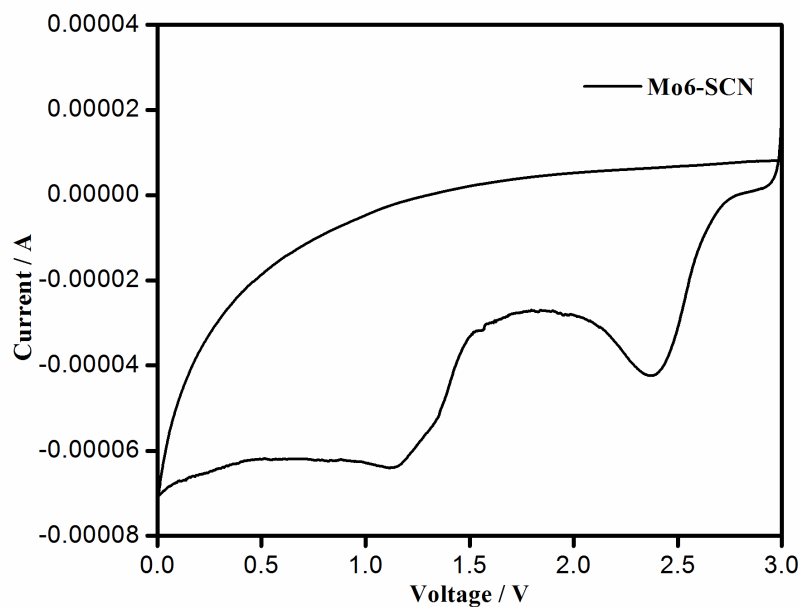


Figure S7. Cyclic Voltammogram for the Mo<sub>6</sub>-SCN in the voltage range of 0-3 V vs. Li/Li<sup>+</sup> at the scan rate of 0.2 mV·s<sup>-1</sup> is showing the reversible electrochemical behavior of Mo<sub>6</sub>-SCN.

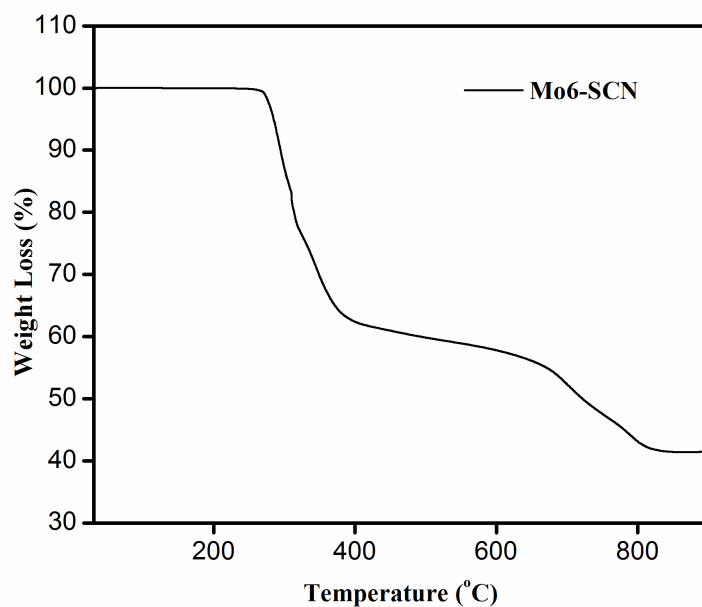


Figure S8. Thermo gravimetric analysis for Mo<sub>6</sub>-SCN, Showing the stability of the Mo<sub>6</sub>-SCN till nearly 300°C then tetrabutyl ammonium cations and organic ligand deteriorated during the course of testing.