

# Inorganic Aromaticity of Mn<sub>6</sub>-Ring Cluster in Layered



Zongxiang Hu<sup>†</sup>, Jiaxin Zheng<sup>†</sup>, Chao Xin<sup>†</sup>, Gaofeng Teng, Yunxing Zuo, and Feng Pan\*

*School of Advanced Materials, Peking University, Shenzhen Graduate School,  
Shenzhen 518055, People ' s Republic of China*

E-mail: 1701111609@ [HYPERLINK "mailto:xxx@xxx.xx" sz HYPERLINK "mailto:xxx@xxx.xx".pku.edu.cn](mailto:xxx@xxx.xx)

Using ab initio calculations, here, we identified inorganic aromaticity of Mn<sub>6</sub>-ring cluster in layered Li(Ni<sub>0.5</sub>Mn<sub>0.5</sub>)O<sub>2</sub> with Ni/Li mixing. The comparison between delocalized orbitals Mn-dz<sup>2</sup> in Mn<sub>6</sub>-ring and benzene-pz uncovers the fundamental similarity between a local cluster and benzene in electronic behavior. We also demonstrate that the delocalized interactions between transition metals (TMs) play a great role in the formation of inorganic aromaticity of Mn<sub>6</sub>-ring in layered TM Li(Ni<sub>0.5</sub>Mn<sub>0.5</sub>)O<sub>2</sub> (with Ni/Li mixing) via a two-level hierarchy: (i) the same TM ions (here manganese) can interact with each other directly through delocalized orbitals Mn-d in Mn<sub>6</sub>-ring, and the local symmetry can impose restrictions on this delocalization. The direct exchange interactions play an important role at this level. (ii) The anions, here oxygen, can match with these delocalized orbitals of d-manifold via bridged bonds to share their electrons with TM ions to create the superexchange interactions, which enable the formation of solid local cluster Mn<sub>6</sub>O<sub>24</sub>. The present findings broaden our knowledge about the interactions between transition metals and provide important factors on governing the local ordering in TM compounds.