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**Five Metal-Organic Frameworks Based on Isomeric Chloro-Functionalized  
Azobenzenedicarboxylic Acids**

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**Abstract**

Chloro-functionalized azobenzenedicarboxylic acids were prepared and their 2D and 3D metal-organic frameworks (MOFs), namely  $\{[\text{Co}(4,4'\text{-Cl}_2\text{abdc})(\text{DMA})]\cdot\text{H}_2\text{O}\}_n$  (**1**),  $\{[\text{Cu}(4,4'\text{-Cl}_2\text{abdc})(\text{DMA})]\cdot\text{G}\}_n$  (**2**),  $\{[\text{Zn}(4,4'\text{-Cl}_2\text{abdc})(\text{DMSO})]\cdot\text{H}_2\text{O}\}_n$  (**3**),  $\{[\text{Mn}(3,3'\text{-Cl}_2\text{abdc})(\text{DMA})]\cdot 0.5\text{DMA}\}_n$  (**4**) and  $\{[\text{Cu}(3,3'\text{-Cl}_2\text{abdc})(\text{DMA})]\cdot 0.5\text{DMA}\}_n$  (**5**), (4,4'-H<sub>2</sub>Cl<sub>2</sub>abdc: 3,3'-dichloro-4,4'-azobenzenedicarboxylic acid, 3,3'-H<sub>2</sub>Cl<sub>2</sub>abdc: 4,4'-dichloro-3,3'-azobenzenedicarboxylic acid), were systematically synthesized to investigate the positional isomer effect on the structures and characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction. The X-ray results demonstrated that **1** and **3** possess a 2-fold interpenetrated 3D+3D→3D framework with the seh-4,6-Imma topology, while **2**, **4** and **5** display 2D layers. In **1** and **3**, infinite [M<sub>2</sub>O(COO)<sub>2</sub>] rod units occur, whilst well-known binuclear [M<sub>2</sub>(COO)<sub>4</sub>] units were observed in the other compounds. **4** and **5** display a lower dimension due to the *cis*-position of the carboxylate groups of 3,3'-Cl<sub>2</sub>abdc as compared to compounds **1-3**, prepared with 4,4'-Cl<sub>2</sub>abdc. Moreover, the thermal, photoluminescence and optical properties of the compounds were also examined.

*Keywords:* chloro-functionalized azobenzenedicarboxylic acid; positional isomer; structural diversity; rod SBU.

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