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EXPLORING ELECTRONIC/SEMICONDUCTING PROPERTIES OF Co, Ni, Mg, Zn-MOF-74s UPON PYRIDINE AND 4-AMINOPYRIDINE ENCAPSULATION

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The rising global demand for sustainable energy has positioned dye-sensitised solar cells (DSCs) as a promising alternative due to low-cost fabrication, environmental friendliness, and adaptability for building-integrated and portable energy solutions. To address the inherent insulating nature of MOF-based materials, this study explores the enhancement of semiconducting properties of M-MOF-74 (M = Co, Ni, Zn, Mg) through vapor-phase encapsulation of electron-rich guest molecules, pyridine and 4-aminopyridine. The successful synthesis and crystallinity of the M-MOF-74s were confirmed by powder X-ray diffraction, which displayed characteristic peaks at 6.7° and 11.7°. Fourier transform infrared spectroscopy revealed blueshifts in the 1700 – 1300 cm^{-1} region, indicating non-covalent interactions and coordination between the guests and open metal sites. Following optical characterisation, these guests improved semiconducting behavior, reducing the band gap of pristine Co-MOF-74 from 2.72 eV to 1.62 eV with 4-aminopyridine and to 2.10 eV with pyridine. Similarly, initial band gaps of Ni-MOF-74 (2.75 eV), Mg (2.86 eV), and Zn (2.87 eV) based analogs demonstrated reductions, while the latter two showed minimal changes due to the closed-shell nature of their metal centres. Cyclic voltammetry (CV) and Mott-Schottky analysis confirmed increased carrier density and retained *n*-type conductivity even after guest encapsulation of all M-MOF-74s. It was found that 4-aminopyridine outperformed pyridine, owing to enhanced electron-donating capability and optimised interaction with the metal centres of MOF. Further, guest encapsulations significantly reduced interfacial resistance and improved electron mobility, thereby confirming the enhancement of interfacial charge transfer. Upon post-modification with pyridine and 4-aminopyridine, Ni-MOF-74 films demonstrated 39% and 7% of power conversion efficiencies (PCE), respectively. In contrast, pyridine and 4-aminopyridine@Mg-MOF-74 showed significant improvements in PCE from 0.25% to 13% along with 17% higher efficiency compared to Co and Zn counterparts in MOF-sensitised photovoltaic devices. This work underscores the potential of pyridine and 4-aminopyridine encapsulated M-MOF-74s, particularly Co- and Mg-MOF-74, as low-cost, tuneable, and efficient materials for next-generation solar energy applications.

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