

## Electronic Structure of Transition-Metal Phthalocyanines from Optimally Tuned Range-Separated Hybrid Functional

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Phthalocyanines are planar and highly symmetric organic molecules that incorporate either two hydrogen atoms (metal-free phthalocyanine H<sub>2</sub>Pc), or one transition metal atom (metal phthalocyanines MPcs) at the center of the ring structure. Physical and chemical properties of MPcs, which are of interest for applications ranging from photovoltaics to spintronics, are strongly dependent on the transition metal *d*-orbital filling. Therefore, understanding MPcs optoelectronic properties requires an accurate description of the *d*-states. In this work, we study the electronic structure and optical excitations of H<sub>2</sub>Pc and MPcs (M=Co, Cu, Ni, Zn), using optimally tuned range-separated hybrid functionals. We provide a systematic analysis of the influences of different fractions of exact exchange in the short-range and long-range interactions on the 3*d*-levels and optical transitions, and their dependence on the *d*-orbital filling of different transition metals. This study highlights the importance of optimal range-separated parameters for describing the 3*d* levels, which is benchmarked with quantum Monte Carlo calculations, and resulting in electronic structures and optical gaps in good agreement with experiments.