

# Nature of C<sub>60</sub> and C<sub>70</sub> fullerene encapsulation in a porphyrin- and metalloporphyrin-based cage: Insights from dispersion-corrected density functional theory calculations

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## Abstract

The search for efficient synthetic hosts able to encapsulate fullerenes has attracted attention with regard to the purification and formation of ordered supramolecular architectures. This study of a porphyrin-based cage as an extension of the well-described ExCage<sup>6+</sup> and BlueCage<sup>6+</sup>, involving viologen as sidearms, provides an interesting scenario where the oblate C<sub>70</sub> fullerene is preferred in comparison to the spherical C<sub>60</sub>. Our results expose the nature of the fullerene-cage interaction involving ~50% of dispersion-type interactions evidencing the strong  $\pi\cdots\pi$  surface stacking, with a complementary contribution by the electrostatic and orbital polarization character produced by a charge reorganization with a charge accumulation facing the porphyrin macrocycles and a charge depletion along the equator formed by the viologens sidearms. Interestingly, the central N<sub>4</sub>H<sub>2</sub> ring from each porphyrin contributes to the dispersion term via N-H $\cdots\pi$  interactions, which is decreased when the metallate N<sub>4</sub>Zn is evaluated. Thus, the formation of stable and selective fullerene encapsulation can be achieved by taking into account two main driving forces, namely, (a) the extension of the  $\pi\cdots\pi$  and X-H $\cdots\pi$  stacking surface and (b) charge reorganization over the fullerene surfaces, which can be used to control fine tuning of the encapsulation thanks to the introduction of more electron-deficient and electron-rich groups within the host cage.