

Visualizing NMR-shielding effect in fullerene-ZnPc aggregates: Characteristic patterns of ZnP-based hosts and encapsulation nature from DFT calculations

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Abstract

The formation of supramolecular aggregates incorporating C_{60} fullerenes can be followed and characterized by nuclear magnetic resonance (NMR) measurements. Here, we unravel the particular patterns provided by zinc-porphyrin (ZnP)-bridged dimers, where the aromatic character of each ZnP unit leads to an enhanced shielding region for the closest fullerene atoms, denoting a slight shielding effect for the equatorial atoms. The nature of the stabilization is discussed and compared to a single ZnP- C_{60} aggregate and a ZnP-dimer (ZnP_2-C_{60}) model, with a significant contribution from noncovalent π - π interactions, allowing us to address the role of bridging chains. The experimental ^{13}C -NMR spectrum of C_{60} in a bridged ZnP dimer shows a single peak owing to the constant tumbling inside the host, which averages the different groups of carbon atoms. The calculations in a static scenario reveal information concerning the local chemical environment underlying the observed shift in relation to isolated C_{60} . We expect that the current approach can be useful to rationalize and predict the origin of the NMR shift upon the formation of host-guest aggregates involving small and large host species.

Author keywords

Fullerenes
host-guest
non-covalent
porphyrin