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Shape-responsive host-guest chemistry: metal-free tetracationic porphyrin nonplanarity promoted by clay mineral interactions assessed by theoretical simulations†



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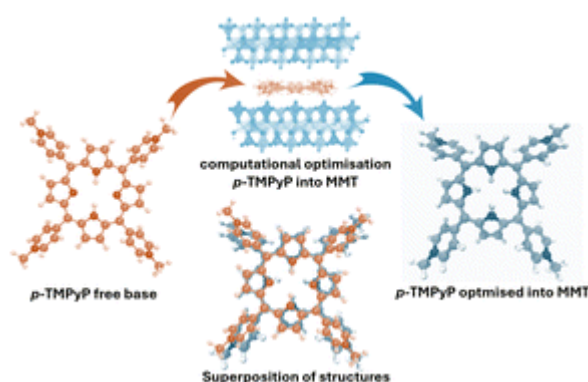
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Abstract

Distortions in the porphyrin core from planarity can trigger a unique structure–property relationship, imparting its basicity, chemical stability, redox potential, and excited-state energetics, among other properties. The colour change promoted by such distortion is signed by red shifts in its electronic absorption spectra. The adsorption of guest *meso*-substituted free-base porphyrin species onto inorganic hosts, such as clay minerals (layered aluminium or magnesium silicates), is known to further promote colour changes. However, the origin of these changes remains a subject of debate without a clear consensus. In this work, an extensive theoretical study was conducted using density functional theory (DFT) to model the interactions between tetracationic porphyrins, specifically *meso*-substituted groups *N*-methyl-4-pyridyl (*p*-TMPyP) and *N*-methyl-3-pyridyl (*m*-TMPyP), and montmorillonite (MMT) with the ideal formula $[(\text{Al}_{1.67}\text{Mg}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2]^{-0.33}$. The following conditions were evaluated: (i) adsorption or intercalation of *p*-TMPyP into MMT host structure, (ii) intercalation of *m*-TMPyP into MMT, and (iii) the influence of water on the intercalation process. The electrostatic interactions between the porphyrins and the MMT siloxane surface induced conformational changes in *p*-TMPyP, characterized by rotation of the substituent groups at the macrocycle periphery and a twist of the porphyrin plane.

The nonplanarity of the intercalated *p*-TMPyP guest produced robust Brønsted basic sites capable of abstracting H⁺ ions from intercalated water molecules, resulting in the formation of a dication. The macrocycle distortion was found to decrease π -conjugation, thereby enhancing the localisation of the lone pair on the imine nitrogen atom. On the other hand, *m*-TMPyP exhibited slight core macrocycle deformations and minor changes in the dihedral angles of its *meso*-substituent groups compared to its isomer, with no observed protonation reaction upon intercalation. These findings highlight the clay microenvironment as a promising strategy for inducing conformational alterations in porphyrins, promoting nonplanarity, and exemplifying a shape-responsive system within the framework of guest–host chemistry.



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