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Abstract

Core Modulation of Porphyrins for Chemical Sensing †

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Abstract: The inner core system of metal-free ('free base') porphyrins has continually served as a ligand for various metal ions, but it was only recently studied in organocatalysis due its highly tunable basicity. Highly conjugated porphyrin systems offer spectrophotometric sensitivity toward geometrical and/or electronic changes and, thus, utilizing the porphyrin core for the selective detection of substrates in solution offers significant potential for a multitude of applications. However, solvation and dilution drastically affect weak interactions by dispersing the binding agent to its surroundings. Thus, the spectroscopic detection of N–H···X-type binding in porphyrin solutions is almost impossible without especially designing the binding pocket. Here, we present the first report on the spectroscopic detection of N–H···X-type interplay in porphyrins formed by weak interactions. Protonated 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetrakis(2-aminophenyl) porphyrin contains coordination sites for the selective binding of charge-bearing analytes, revealing characteristic spectroscopic responses. While electronic absorption spectroscopy proved to be a particularly useful tool for the detection of porphyrin–analyte interactions in the supramolecular complexes, X-ray crystallography helped to pinpoint the orientation, flexibility, and encapsulation of substrates in the corresponding atropisomers. This charge-assisted complexation of analytes in the anion-selective porphyrin inner core system is ideal for the study of atropisomers using high-resolution NMR, since it reduces the proton exchange rate, generating static proton signals. Therefore, we were able to characterize all four rotamers of the nonplanar 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetrakis(2-aminophenyl) porphyrin by performing 1D and 2D NMR spectroscopic analyses of host-guest systems consisting of benzenesulfonic acid (BSA) and each porphyrin atropisomer. Lastly, a detailed assignment of the symmetry operations that are unique to porphyrin atropisomers allowed us to accurately identify the rotamers using NMR techniques only. Overall, the N–H···X-type interplay in porphyrins formed by weak interactions that form restricted H-bonding complexes is shown to be the key to unravelling the atropisomeric enigma.

Keywords: porphyrins; sensing; atropisomers; NMR; UV–vis; nonplanar

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