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Section: Materials for Chemical Sensing

Core Modulation of Porphyrins for Chemical Sensing

The inner core system of metal-free ('free base') porphyrins has continually served as a ligand for various metal ions, but only recently was studied in organocatalysis due its highly tuneable basicity. Highly conjugated porphyrin systems offer spectrophotometric sensitivity towards geometrical and/or electronic changes and thus, utilizing the porphyrin core for 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, spectroscopic detection of N–H···X-type binding in porphyrin solutions is almost impossible without specially designing the binding pocket.

Here we present the first report on spectroscopic detection of the 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 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 by 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, 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 shows to be the key to unravel the atropisomeric enigma.