

Rigid and Flexible Bis-Porphyrinic Tweezers : Efficient Molecular Recognition of Bidentate Bases.

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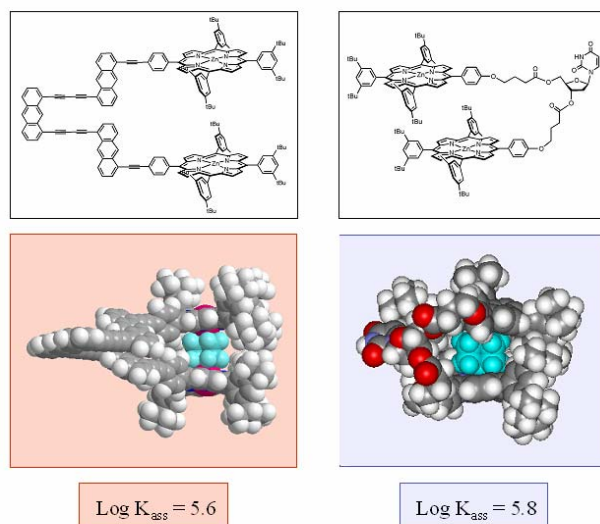
Increasing efforts are devoted to the synthesis of cofacial bis-porphyrinic tweezers able to complex various bidentate guests through axial coordination of the Zn(II) porphyrins by the two nitrogen atoms.¹ Elaboration of rigid receptors appeared up to now as the ideal way to pre-organize a bis-porphyrinic cavity and increase the stability of the formed host/guest complexes. However, the choice of using rigid spacer to attach the two porphyrins together may cost a lot as far as solubility and stability are concerned. The synthetic pathways necessary to achieve the synthesis of rigid systems are frequently long and tedious. We report here the synthesis and studies of new flexible bis-porphyrinic tweezers bearing uridine as linkers and offering pre-organized cavities able to welcome bidentate guests with extremely high association constants.

As part of our studies concerning complexation of bidentate Lewis bases by bis-porphyrinic tweezers,² we have synthesized two new bis-porphyrins bearing a flexible nucleosidic linker.³ Both uridine and 2'-deoxyuridine spacers were chosen on account of some observations we made a few years ago on the unexpected blocked conformations adopted by a pentaporphyrin consisting of four Zn(II) porphyrins attached to a central free-base porphyrin by four nucleosidic linkers.⁴ Since we observed no such blocked conformations in other flexible pentaporphyrins,⁵ we thought this might be due to the nucleosidic nature of the linkers. We thus synthesized two dimers, which differ by the attachment positions of the two porphyrins.

The ability of these two tweezers to accommodate guests was investigated through ligand binding studies carried out in dichloromethane with DABCO as bidentate base. The complexation of DABCO by these dimers was monitored by UV-visible spectrophotometric titration in CH₂Cl₂. The binding constants between these two tweezers and DABCO were calculated from UV-visible spectroscopic data. These association constants are unexpectedly increased by more than one order of magnitude as compared to the association constants of the same bidentate ligand with a reference Zn(II) mono-porphyrin. This enhanced stability of the complexes may be ascribed to a pre-organization of the bis-porphyrinic tweezers forming a cavity, and provides convincing evidence that the bidentate base is inserted into the cavity of the dimers *via* host/guest interactions.

We demonstrated that similar association constants can be obtained with flexible tweezers bearing uridine as linker and rigid tweezers. However, the stability of these flexible complexes isn't as convincing as for our rigid tweezers bearing a tris-anthracenic spacer since the addition of an excess of DABCO destroys all the flexible complexes.

Molecular modelling of one of the flexible tweezers and its 1/1 complex with DABCO is represented below, as well as our rigid tweezers bearing a tris-anthracenic spacer.



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References

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