A Supramolecular Cup-and-Ball C_{60}-Porphyrin Conjugate System.

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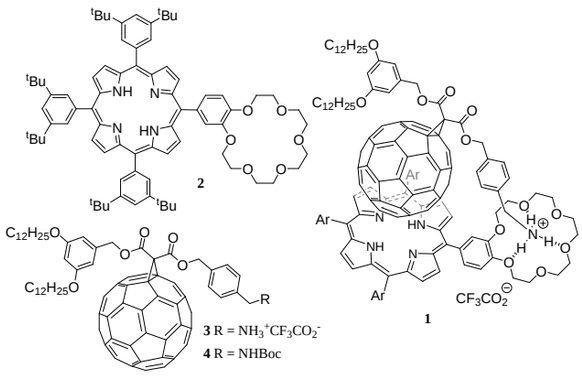
Photophysical properties of porphyrin-linked fullerene hybrids have received considerable attention in the last few years.[1] In order to understand the nature of the dialog among the C_{60} and the porphyrin chromophores, the topology of the two moieties in dyads has been systematically varied and a wide range of covalent assemblies have been reported.[1] A few examples of supramolecular C_{60}-porphyrin conjugates have also been described so far.[2-3] In most cases, these non-covalent assemblies have been obtained from a C_{60} derivative bearing a pyridyl moiety and a metalloporphyrin through coordination to the metal ion. Due to the apical binding on the porphyrin subunit, the attractive van der Waals interaction of the fullerene sphere with the planar π-surface of the porphyrin seen for several covalent C_{60}-porphyrin derivatives[4] is not possible in such arrays. We have demonstrated that π-stacking of the two chromophores can have a dramatic effect on the recognition interactions in non-covalent C_{60}-porphyrin ensembles.[5] Specifically, supramolecular complex **1** has been obtained from porphyrin-crown ether conjugate **2** and methanofullerene derivative **3**[6] bearing an ammonium function. In addition to the ammonium-crown ether interaction, intramolecular stacking of the fullerene moiety and the porphyrin subunit has been evidenced in **1**. Due to this additional recognition element, the association constant (K_a) for the complex obtained from **2** and **3** is increased by two orders of magnitude when compared to K_a values previously found for the complexation of **3** with other crown ether derivatives.[6] In this paper, we will report on our latest advances in this field.



Acknowledgements
This work was supported by the CNRS and the French Ministry of Research.

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