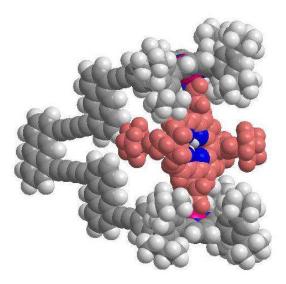
Adjustable Cavity in Cofacial Bisporphyrinic Tweezers for the Recognition of PhotoActive Guests.

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In photosynthetic systems, the energy contained in a single photon is transferred in a very short time and with minimal loss from the point where it is absorbed to where it is needed. This extraordinary efficiency is ascribed to the favored spacing and orientation of the bacteriochlorophylls constituting the light harvesting pigments, which are held in an appropriate parallel conformation by short polypeptides.¹

As part of our work on the synthesis of molecular wires bearing pendant porphyrins for the study of exciton migration and the obtaining of self-coordinated molecular systems with predictable spectral and redox characteristics,2 we investigated the modulation of the physico-chemical properties of cofacial bis-porphyrinic tweezers by host/guest interactions. We recently evidenced that an electronic coupling was generated between the two porphyrins of such a small tweezers when a molecule of pyrazine was inserted into the cavity generating a 1/1 host/guest complex.³ The enhanced stability observed in the complexation of pyrazine by that dimer was ascribed to the preorganization of the Zn(II) bis-porphyrin. The synthesis of a rigid cofacial bisporphyrinic tweezers bearing a tris-anthracenic spacer has then been carried on. Its behavior as host has been evidenced as well as the ability of its cavity to adjust to guests of various sizes.4 A tris-anthracenic spacer was chosen in order to keep a cofacial orientation of the chromophores while allowing a free rotation along the acetylenic axis to adjust the size of the cavity to a large variety of guests.



This rigid tweezers is able to coordinate a free-base trans-

dipyridyl-porphyrin to generate a supramolecular complex with a high association constant (K_a = 10^6M^{-1}). After selective irradiation of the tris-anthracenic spacer, an energy transfer occurs from the excited host towards the complexed free-base guest porphyrin.⁵

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References

- a) J. Barber, B. Andersson, Nature 1994, 370, 31-34.
 b) W. Kühlbrandt, Nature 1995, 374, 497-498.
 c) G. McDermott, S. M. Prince, A. A. Freer, A. M. Hawthornthwaite-Lawless, M. Z. Papiz, R. J. Cogdell, N. W. Isaacs, Nature 1995, 374, 517-521.
 d) T. Pullerits, V. Sundström, Acc. Chem. Res. 1996, 29, 381-389.
- a) N. Solladié, A. Hamel, M. Gross, Tetrahedron Lett. 2000, 41, 6075-6078. b) N. Aubert, V. Troiani, M. Gross, N. Solladié, Tetrahedron Lett. 2002, 43, 8405-8408.
- 3. J. Brettar, J. P. Gisselbrecht, M. Gross, N. Solladié, Chem. Commun. **2001**, 733-734.
- R. Rein, M. Gross, N. Solladié, Chem. Commun. 2004, 1992-1993.
- 5. L. Flamigni, A. M. Talarico, B. Ventura, R. Rein, N. Solladié, Chemistry, A Eur. J. **2005**, in press.