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Adjustable cavity for host–guest recognition in cofacial bis-porphyrinic tweezer

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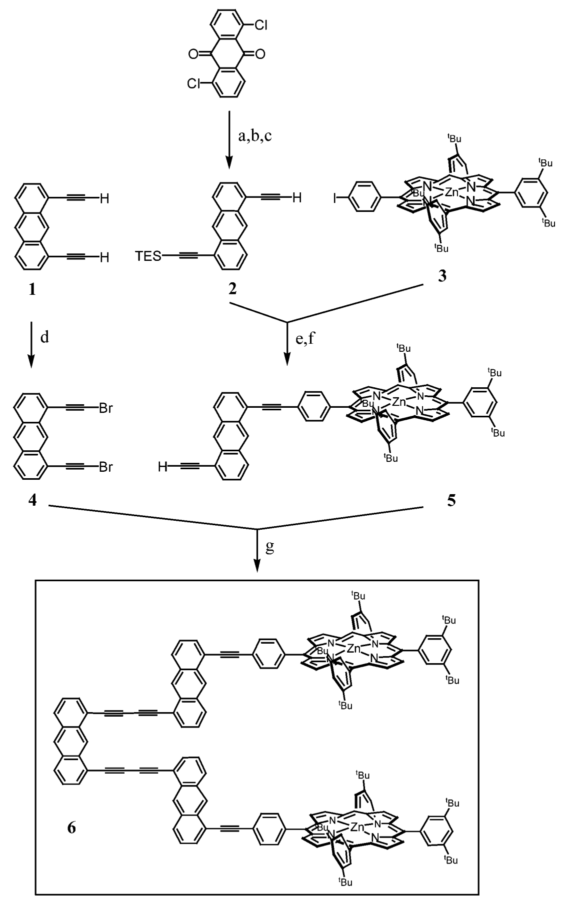
The synthesis of a cofacial bis-porphyrinic tweezer bearing a tris-anthracenic spacer is reported. Its behavior as host has been evidenced as well as the ability of its cavity to adjust to guests of various sizes.

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 tweezer by host–guest interactions.[3] We recently proved that an electronic coupling was generated between the two porphyrins of such a small tweezer when a molecule of pyrazine was inserted into the cavity generating a 1 : 1 host–guest complex.[4] The enhanced stability observed in the complexation of pyrazine by that dimer was ascribed to the preorganization of the Zn(II) bis-porphyrin. We now report the synthesis of a new extended cofacial bis-porphyrinic tweezer **6** bearing an adjustable cavity. Specifically, a tris-anthracenic spacer was chosen in order to facilitate a cofacial orientation of the chromophores while allowing a free rotation around the acetylenic axis, thus adjusting the cavity to a large variety of guests.

The synthesis of dimer **6** is described in Scheme 1. It relies upon the cross-coupling of two porphyrin–anthracene conjugates (**5**) on a central 1,8-dibromoacetylene-anthracene. This synthesis is based on the anchoring of two acetylenic functions at different positions of the anthracene. This is exemplified in the central linker **4** which bears dibromoacetylenes at the C-1 and C-8 positions, while the precursor **2** has C-1 and C-5 substituents. Compound **4** was obtained by bromination of 1,8-diethynylanthracene **1**,[5] which has been previously reported.[4] The dissymmetrical 1-ethynyl-5-triethylsilylethynyl-anthracene **2** was prepared from the commercially available 1,5-dichloroanthraquinone in three steps. The latter was first reduced using zinc powder.[6] The resulting 1,5-dichloroanthracene was then reacted with triethylsilylacetylene magnesium bromide in THF in the presence of PPh_3 and $Ni(acac)_2$ under reflux for 3 days.[7] **2** was finally obtained by statistical deprotection of one triethylsilyl protecting group. This reaction yielded 43% of the desired product **2**, 16% of the fully deprotected compound and 33% of unreacted starting material. A Sonogashira coupling reaction was, at that stage, carried out between the free acetylene **2** and the iodo-porphyrin **3**.[8] **5** was obtained by subsequent deprotection of the triethylsilyl group under classical basic conditions. The desired tweezer **6** was finally obtained by coupling two porphyrinic arms **5** to the central 1,8-dibromoacetylene-anthracene linker **4**. Major difficulties were encountered during this step due to the formation of the homo-coupling product. The hetero-coupling conditions developed by Vasella and Cai gave the best results for the present purpose.[9] The desired bis-porphyrinic tweezer **6** was finally isolated in 33% yield.†

The tris-anthracenic spacer allows a free rotation around the acetylenic axis thus contributing to adjust the size of the cavity to a large variety of guests. The ability of **6** to accommodate various guests was investigated through binding studies carried out in dichloromethane with three bidentate bases of different lengths and pK_a, namely pyrazine, DABCO and 4,4′-bipyridine. The complexation was monitored by UV–visible spectrophotometric titration of a solution of dimer **6** in CH_2Cl_2 with pyrazine (Fig. 1, [**6**] = 6 10^{-5} M), DABCO ([**6**] = 4.5 10^{-5} M) or 4,4′-bipyridine ([**6**] = 3 10^{-5} M), which resulted as expected in significant red-shift of the Soret and Q bands in the porphyrins.[10] Clear isosbestic points indicated in all cases an equilibrium between two defined species.

Association constants (K_a) between tweezer **6** and pyrazine, 4,4′-bipyridine and DABCO were calculated from UV–visible spectroscopic data and values of respectively $10^{3.9}$ M^{-1}, $10^{4.6}$ M^{-1} and $10^{5.6}$ M^{-1} were found. These three association constants are increased by one order of magnitude when compared to the association constants of the same bidentate ligands with a reference



Scheme 1 *Reagents and conditions*: a) Zn, NH_3aq., then HCl, *i*-PrOH, 41%. b) TESCCMgBr, PPh_3, $Ni(acac)_2$, THF, reflux, 25%. c) K_2CO_3, THF–CH_3OH 85 : 15, rt, 6 h 30, 43%. d) NBS (2.4 eq.), $AgNO_3$ (0.12 eq.), acetone, rt, 4 h, 87%. e) $Pd(PPh_3)_2Cl_2$, CuI, NEt_3, rt, 24 h, 58%. f) K_2CO_3, THF–CH_3OH 50 : 50, rt, 6 h, 87%. g) $Pd_2(dba)_3$ (0.02 eq.), CuI (0.025 eq.), LiI (0.2 eq.), PMP (2.8 eq.), DMSO, rt, 3 days, 33%.

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Zn(II) porphyrin 5,10,15,20-tetra-di-*tert*-butyl-phenyl-porphyrin **A_4** ($10^{2.7}$ M^{-1}, $10^{3.6}$ M^{-1} and $10^{4.4}$ M^{-1}), in spite of the difference in size and pK_a of the guest involved in this recognition process. This enforced stability of such complex may be ascribed to the pre-organization of the bis-porphyrinic tweezer **6**. It provides convincing clues that the bidentate bases are inserted into the cavity of the dimer *via* host–guest interactions.

Plotting the variation of the absorbance *versus* the number of added equivalents of Lewis base per porphyrin evidenced that full complexation was achieved faster for the complexes between tweezer **6** and the three studied guests than for the complexes between the same Lewis bases and the reference monoporphyrin **A_4** (Fig. 2). In particular, no further modification of the absorbance was observed beyond the concentrations ratio 1 : 1 for both DABCO–**6** and 4,4′-bipyridine–**6**, thus providing further evidence that the complexation occurred with an exact 1 : 1 stoichiometry between host and guest in both cases. These results clearly confirm that one guest molecule, either DABCO or 4,4′-bipyridine, was inserted into the cavity of the porphyrin dimer **6**, yielding a 1 : 1 host–guest complex, and they document the adjustability of the host's cavity to the size of the guest to be accommodated.

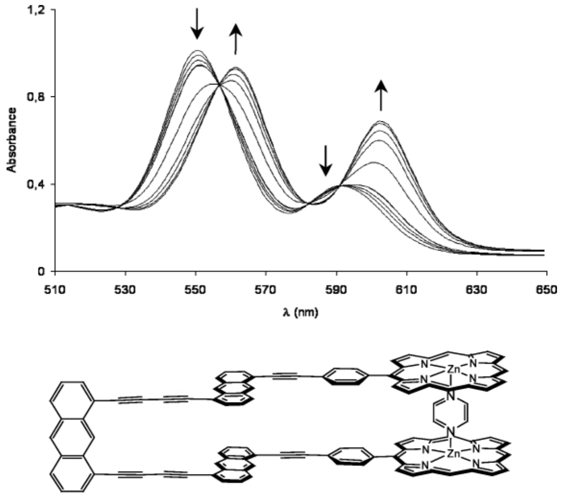

Fig. 1 UV–vis spectroscopic titration of **6** with pyrazine in CH_2Cl_2 at rt. Spectral changes of **6** on addition of pyrazine at rt: [**6**] = 6 10^{-5} M, concentrations ratio = [pyrazine] : [**6**] = 0; 0.8; 1; 1.6; 3; 6.5; 12.5; 25; 40.

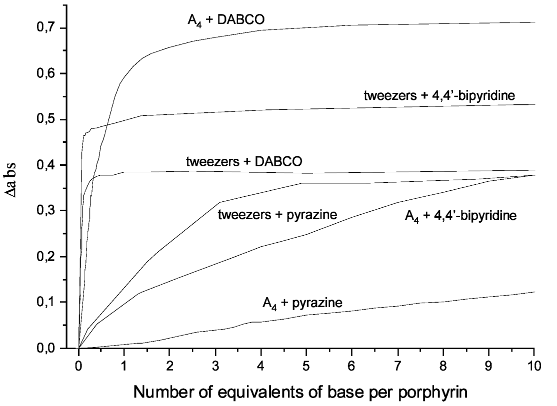

Fig. 2 Plot of the variation of the absorbance versus the number of equivalents of Lewis base added per porphyrin. Full complexation is reached for concentrations ratio 1 : 1 for tweezer–DABCO or tweezer–4,4′-bipyridine (*i.e.* 2 : 1 for porphyrin–DABCO and porphyrin–4,4′-bipyridine).

In summary, a new extended cofacial bis-porphyrinic tweezer **6** bearing an adjustable cavity was synthesized. A tris-anthracenic spacer was chosen to facilitate a cofacial orientation of the chromophores while allowing a free rotation around the acetylenic axis, thus contributing to adjust the size of the cavity to guests such as pyrazine, DABCO and 4,4′-bipyridine. The formation of 1 : 1 host–guest complexes **6**–DABCO or **6**–4,4′-bipyridine by insertion of the Lewis base into the cavity of the dimer was demonstrated, evidencing the feasibility of the recognition process *via* adjustment of the host's cavity to the size of the guest.

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Notes and references

† Selected spectroscopic data for **6**: ^{1}H NMR ($CDCl_3$, 300 MHz) : δ (ppm) : 9.78 (s, 1H, H_9), 8.93 (d, 4H, H_β, ^3J = 4.7 Hz), 8.91 (d, 4H, H_β, ^3J = 4.8 Hz), 8.89 (d, 4H, H_β, ^3J = 4.4 Hz), 8.88 (d, 4H, H_β, ^3J = 4.6 Hz), 8.81 (s, 2H, $H_{9' \text{ or } 10'}$), 8.80 (s, 2H, $H_{9' \text{ or } 10'}$), 8.57 (s, 1H, H_{10}), 8.25 (d, 4H, $H_{o''}$, ^3J = 8.2 Hz,), 8.13 (d, 4H, $H_{m''}$, ^3J = 8.4 Hz), 8.13 (d, 2H, $H_{8'}$, hidden), 8.13 (d, 2H, $H_{4'}$, hidden), 7.99 (d, 4H, H_o, ^4J = 1.7 Hz), 7.98 (d, 2H, $H_{6'}$, ^3J = 7.2 Hz), 7.92 (d, 8H, $H_{o'}$, ^4J = 1.4 Hz), 7.90 (d, 2H, $H_{2'}$, ^3J = 6.6 Hz), 7.89 (d, 2H, $H_{4\text{–}5}$, ^3J = 8.9 Hz), 7.75 (t, 2H , H_p, ^4J = 1.7 Hz), 7.63 (t, 4H , $H_{p'}$, ^4J = 1.8 Hz), 7.57 (dd, 2H, $H_{7'}$, ^3J = 8.5 Hz, ^3J = 7.0 Hz), 7.49 (dd, 2H, $H_{3'}$, ^3J = 8.6 Hz, ^3J = 7.0 Hz), 7.26 (d, 2H, $H_{2\text{–}7}$, hidden), 6.95 (dd, 2H, H_3, ^3J = 8.5 Hz, ^3J = 7.0 Hz), 1.49 (s, 36H, *t*-Bu), 1.35 (s, 72H, *t*-Bu); UV–vis λ_{max} (CH_2Cl_2)/nm : 265 (134700), 426 (505500), 552 (23700), 594 (10900); MS (FAB^+) : m/z = 2700.3 ($[M]^+$, calcd: 2700.3).

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