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Tweezers hosts for intercalation of Lewis base guests: Tuning physico-chemical properties of cofacial porphyrin dimers

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The synthesis and both spectroscopic and electrochemical studies of a bis-porphyrinic tweezer are reported, as well as the insertion of Lewis base guests into the host bis-porphyrinic cavity, monitored through physico-chemical characteristics.

In natural 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.[1]

Increased efforts have been developed towards understanding this great efficiency and many multi-porphyrinic devices have been synthesized as potential models of the natural system.[2] One possible approach for the preparation of such devices is to force the cofacial orientation of the porphyrins *via* the use of a rigid spacer.[3] With the aim of identifying an optimized spacer for the construction of photonic and electronic wires, we first focused on the study of a cofacial porphyrin dimer.[4] We now report how the insertion of a pyrazine molecule into the cavity of a Zn(II) porphyrin dimer through host–guest interactions causes an electronic coupling between the two porphyrin chromophores.

A 1,8-diethynylanthracenic spacer has been chosen for its expected ability to hold two chromophores in a cofacial orientation and for synthetic reasons as well. Indeed, the use of a Sonogashira coupling reaction between the diacetylene **1** and the iodoporphyrin **2**[5] allowed the efficient synthesis of dimer **3a** in four steps starting from commercially available compounds (Fig. 1).[6] The free-base dimer **3b** was obtained in 89% yield by demetallation of the two porphyrins under acidic conditions.[7]

UV-visible spectra of the reference porphyrins, the Zn(II) and free-base 5,10,15,20-tetra(3,5-di-*tert*-butylphenyl)porphyrins **4a–b**, and both dimers **3a** and **3b** were recorded in CH$_2$Cl$_2$ solutions. Only a small blue shift (2 nm for free-base compounds and 3 nm for metallated porphyrins) as well as a tiny broadening of the Soret band could be noticed from the monomer to the dimer, indicating that almost no coupling exists between the two porphyrins.

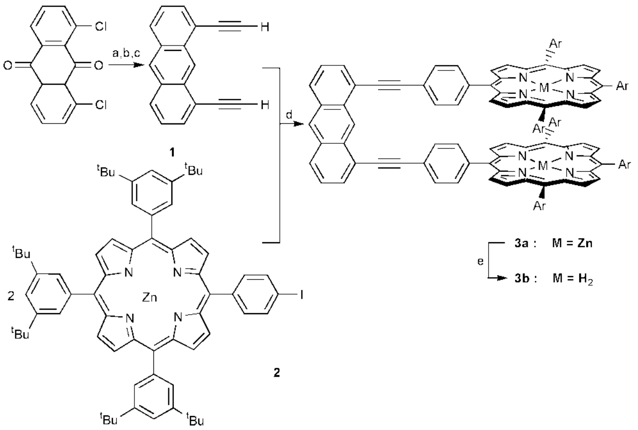

Fig. 1 (a) Zn, NH$_3$aq., then HCl, *i*-PrOH, 36%; (b) TMSCCMgBr, PPh$_3$, Ni(acac)$_2$, THF, reflux, 75%; (c)K$_2$CO$_3$, THF–CH$_3$OH 85:15, 61%; (d) Pd(PPh$_3$)$_2$Cl$_2$, CuI, NEt$_3$, 63%; (e) TFA in CH$_2$Cl$_2$, 89%. Ar = 3,5-di-*tert*-butylphenyl.

Fluorescence measurements were carried out in CH$_2$Cl$_2$ on both dimers **3a–b**, and also on the spacer **1** and on the reference porphyrins **4a–b**. Upon almost selective excitation of the anthracene moiety at 267 nm in the free-base dimer **3b**, only the fluorescence of the two porphyrins could be detected, indicating a total quenching of the emission from the anthracenic moiety. The assumption of an energy transfer from anthracene to the adjacent porphyrins was corroborated by the registration of the excitation spectrum of the dimer **3b**, which matches the absorption of the multicomponent system. A similar energy transfer from anthracene towards the adjacent chromophores was also observed upon irradiation of the Zn(II) dimer **3a** but the quantum yield was smaller and the fluorescence of the anthracenic sub-unit still remains the main deactivation pathway.

We investigated also the possible generation of host–guest complexes between the Zn(II) bis-porphyrin **3a** and small bidentate ligands bearing two nitrogen atoms.[4] Pyrazine and DABCO (1,4-diazabicyclo[2.2.2]octane) were chosen as first examples because of their fairly different p*K*a values (respectively 0.6 and 3). The coordination was monitored by ^{1}H NMR and UV-visible absorption spectroscopies in order to determine, in particular, the stoichiometry of the complexes, and the effects of such coordination on the characteristics of the porphyrin dimer.

The complexation was first studied by ^{1}H NMR (300 MHz) titration of dimer **3a** with pyrazine in CDCl$_3$. Upon addition of increasing amounts of pyrazine to a 2.10^{-3} M solution of porphyrin dimer **3a**, changes in the chemical shifts were observed up to a concentration of pyrazine equal to one equiv. of **3a** and no further changes beyond. This strongly suggests that a 1:1 complex was created between pyrazine and porphyrin dimer **3a**. Further indications on this complexation were obtained from UV-visible spectrophotometric titrations of a 2.10^{-5} M solution of dimer **3a** in CH$_2$Cl$_2$ with pyrazine (Fig. 2): such a titration of **3a** with pyrazine resulted in significant red-shift of the Soret and Q bands in the porphyrins,[8] and the titration curves obtained from absorption changes at 562 nm (Q band) exhibited a sharp saturation beyond the concentrations ratio 1:1 for pyrazine–**3a**. The titration data and the observed isosbestic points clearly indicated the existence of an equilibrium between two defined species, thus leading to the conclusion that a 1:1 complex was formed between dimer **3a** and pyrazine, with an association constant of 10$^{5.6}$ M^{-1}.[9] In contrast, there was no experimental evidence of any appreciable complex formation between the reference porphyrin **4a** and pyrazine at such low concentrations by either UV-visible or ^{1}H NMR spectroscopies. These results clearly indicated that the pyrazine molecule was inserted into the cavity of the porphyrin dimer **3a**, yielding a 1:1 host–guest complex.

Titration of **3a** with DABCO and the absence of complexation between the latter and the reference porphyrin **4a** until a

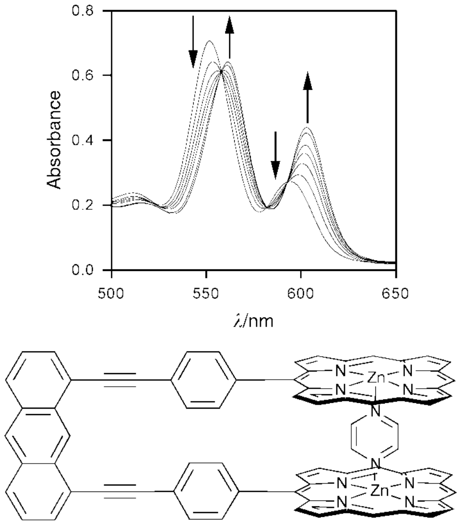

Fig. 2 UV-vis spectroscopic titration of **3a** with pyrazine in CH$_2$Cl$_2$ at rt. Spectral change of **3a** on addition of pyrazine at rt: [**3a**] = 2.10^{-5} M, concentrations ratio = [pyrazine]:[**3a**] = 0; 0.2, 0.4, 0.6, 0.8, 1, 2. 3,5-Di-*tert*-butylphenyl substituents on the porphyrins have been omitted for clarity.

concentrations ratio of DABCO–**4a** = 10:1, produced similar conclusions as above with pyrazine. A 1:1 host–guest complex was created by insertion of one DABCO molecule into the cavity of each porphyrin dimer **3a**, with an association constant of 10^7 M^{-1}.[9]

Electrochemical studies were carried out on a glassy carbon working electrode in CH$_2$Cl$_2$ + 0.1 M Bu$_4$NPF$_6$. Cyclic voltammetry exhibited, for the porphyrin dimer **3a**, two reversible oxidation steps as well as a third, irreversible oxidation and three reversible reduction steps at respectively −2.30 (2e$^-$), −2.10 (1 e$^-$), −1.86 (2 e$^-$), +0.32 (2 e$^-$), +0.64 (2 e$^-$) and +0.95 V *vs.* Fc$^+$/Fc. Assignments of the different steps were made by comparison with the redox pattern of the building blocks, namely anthracene **1** and porphyrin **4a**, whose redox characteristics are summarised in Table 1.

Analysis of the electrochemical results revealed that the reversible one electron reduction of **3a** at −2.10 V and the irreversible oxidation at +0.95 V *vs.* Fc$^+$/Fc occur on the anthracene linker. The remaining four electron transfers each involve two one-electron reversible transfers occurring on the two porphyrin units. The peak shape and characteristics of the cyclic voltammograms indicated that the two porphyrins behave in **3a** as independent redox centers as expected from the large ring–ring distance (*ca.* 5.8 Å, according to molecular modelling). Such a distance makes unlikely any interaction between the two porphyrin rings.

In the presence of increasing amounts of pyrazine, the cyclic voltammograms of **3a** were modified up to a pyrazine–**3a** ratio of 1, in agreement with the UV-visible titrations. The resulting complex gave well resolved cyclic voltammograms where the first oxidation and the first reduction steps each became split into two distinct one-electron reversible steps at respectively −1.87 and −1.95 V *vs.* Fc$^+$/Fc and +0.28 and +0.40 V vs. Fc$^+$/Fc.[10] Such a behavior is characteristic of a porphyrin–porphyrin interaction. This experimental observation unambiguously indicated that it is possible to modify the electron transfer pattern of the dimer **3a** by host–guest interactions, as documented for instance in the present paper, by intercalating one pyrazine molecule into the cavity of the bis-porphyrinic tweezer **3a**. Both spectroscopic and electrochemical studies on the complexation of either pyrazine or DABCO Lewis bases by the porphyrin dimer **3a** revealed that no further spectral or voltamperogram changes occurred beyond a concentrations ratio Lewis base–**3a** = 1:1.

Table 1 Redox potentials in CH$_2$Cl$_2$ + 0.1 M Bu$_4$NPF$_6$ obtained by cyclic voltammetry on a glassy carbon working electrode. All potentials are given *vs.* ferrocene used as internal standard. Pyrazine is not electroactive in the available potential range

Species	Reduction *E* (V *vs.* Fc$^+$/Fc)				Oxidation *E* (V *vs.* Fc$^+$/Fc)			
1		−2.08 (1 e$^-$)						+0.97 (irrev.)
4a	−2.25 (1 e$^-$)			−1.85 (1 e$^-$)	+0.35 (1 e$^-$)		+0.67 (1 e$^-$)	
3a	−2.30 (2 e$^-$)	−2.10 (1 e$^-$)		−1.86 (2 e$^-$)	+0.32 (2 e$^-$)		+0.64 (2 e$^-$)	+0.96 (irrev.)
3a + **pyrazine**		−2.07 (1 e$^-$)	−1.95 (1 e$^-$)	−1.87 (1 e$^-$)	+0.28 (1 e$^-$)	+0.40 (1 e$^-$)	+0.75 (2 e$^-$)	+0.95 (irrev.)

The above results clearly indicated that each bidentate Lewis base (pyrazine and DABCO) was inserted into the cavity of the porphyrin dimer **3a**, generating a 1:1 host–guest complex. The enhanced stability observed in the complexation of the bidentate bases by the dimer **3a** (if compared with the complexation of the same bases by the reference porphryin **4a**) may be ascribed to the preorganization of the Zn(II) bis-porphyrin **3a**. The spectrometric and electrochemical results revealed that the 1:1 host–guest complex generated between **3a** and the pyrazine molecule enabled the two porphyrins to undergo an electronic coupling. Such changes in the spectroscopic and electrochemical properties of cofacial porphyrin dimers by host–guest interactions pave the way towards self-coordinated molecular systems with predictable spectral and redox characteristics. Work is in progress on this subject.

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