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Restricted rotation in a tetrakis(*para*-substituted phenyl) porphyrin bearing four porphyrin–fullerene substituents

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Abstract—A porphyrin substituted with four porphyrin–fullerene moieties has been prepared and variable-temperature NMR studies revealed a high barrier to free rotation about the four *para*-substituted phenyl groups of the central porphyrin core.

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Owing to their electronic properties, porphyrins and fullerenes are interesting complementary building blocks for the preparation of artificial photosynthetic systems and molecular photonic devices.[1] Indeed, many examples of covalently linked porphyrin–fullerene derivatives have been described in the past years.[1] Their photophysical properties have been investigated in detail and the intramolecular processes such as electron and energy transfer evidenced in such multicomponent hybrid systems.[1] On the other hand, C_{60}–porphyrin conjugates have also revealed unique conformational properties resulting either from the attractive van der Waals interaction of the fullerene sphere with the planar π-surface of the porphyrin[2] or from the symmetry of the C_{60} derivative attached to the porphyrin unit.[3,4] For example, porphyrin derivatives bearing two 1,3-phenylenebis(methylene)-tethered fullerene cis-2 bis-adduct subunits have been obtained as mixtures of two conformers and NMR studies revealed an original dynamic cis/trans isomerization.[3] Following this first example of atropisomerism in bis(*meta*-substituted phenyl) porphyrins, few other examples of related porphyrins for which the barrier to free rotation is high enough to distinguish the cis and trans conformers have been described.[5] As part of this research, we now report the synthesis and the characterization of compounds **1** and **2** (Fig. 1) which are, to the best of our knowledge, the first tetrakis(*para*-substituted phenyl)porphyrins for which a high barrier to free rotation is evidenced.

To fully understand the dynamic properties of compounds **1** and **2**, model C_{60}–porphyrin conjugate **4** and the corresponding Zn(II) complex (**5**) were prepared and investigated first. The condensation of **3**[4] (1 equiv), mesitaldehyde (3 equiv) and pyrrole (4 equiv) was performed in $CHCl_3$ (commercial $CHCl_3$ containing 0.75% ethanol as stabilizer) at room temperature in the presence of $BF_3 \cdot Et_2O$ under the reaction conditions developed by Lindsey for the synthesis of sterically hindered porphyrins[6] (Scheme 1). After 2 h, *p*-chloranil was added to irreversibly convert the porphyrinogen to the porphyrin. The desired fullerene–porphyrin conjugate **4** was isolated in 11% yield by chromatographic separations. Subsequent metalation with $Zn(OAc)_2$ gave **5** in 84% yield. The MALDI-TOF mass spectrum of both **4** and **5** shows the expected molecular ion peak at *m*/*z* 2607.4 ($[M]^+$, calcd for $C_{183}H_{160}N_4O_{12}$: 2607.21) and 2669.6 ($[M]^+$, calcd for $C_{183}H_{158}N_4O_{12}Zn$: 2669.12), respectively. The ^1H NMR spectra of both **4** and **5** recorded at room temperature are in full agreement with their C_s symmetric structures imposed by the 1,3-phenylenebis(methylene)-tethered fullerene cis-2 bis-adduct subunit (Fig. 2). Interestingly, the spectra revealed three sets of signals for the mesityl groups. Indeed, molecular modelling studies on compound **5** show that the fullerene substituent is located to one side of the plane of its bridging phenyl ring. Therefore, due to the high barrier to rotation of this phenyl substituents on the porphyrin, the three mesityl groups are different. A variable-temperature NMR study ($C_2D_2Cl_4$, 250 MHz) showed a clear coalescence and confirmed the restricted rotation of the 3,5-substituted phenyl substituent on the porphyrin ring. The activation free energy of the

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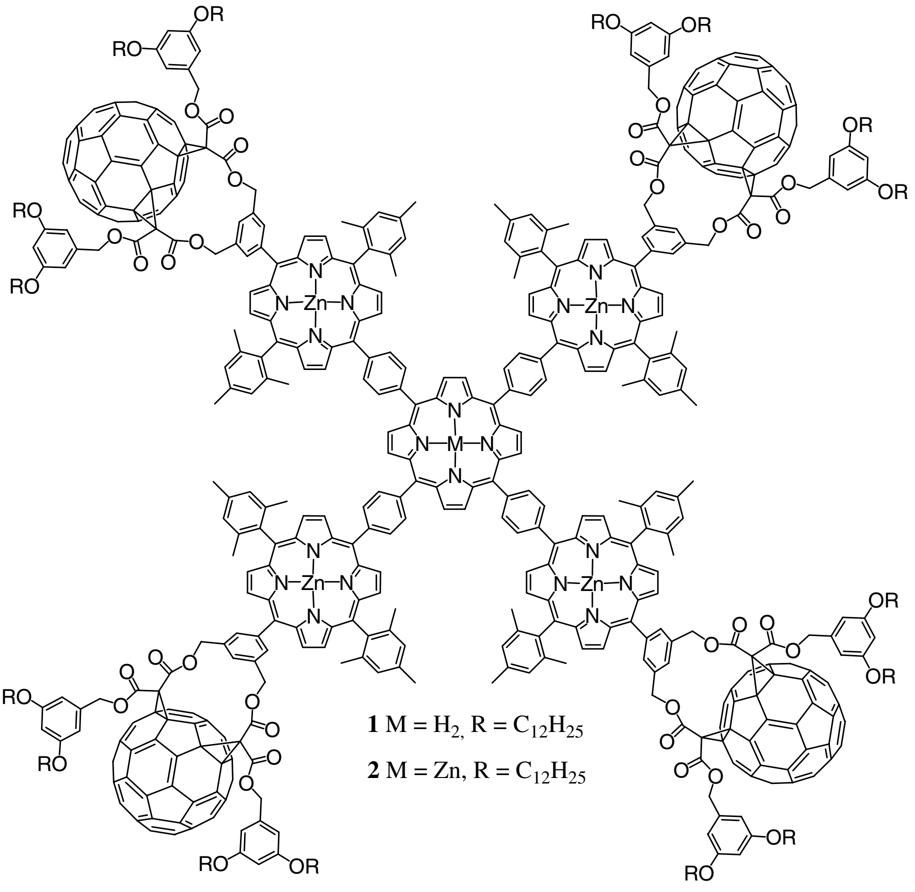
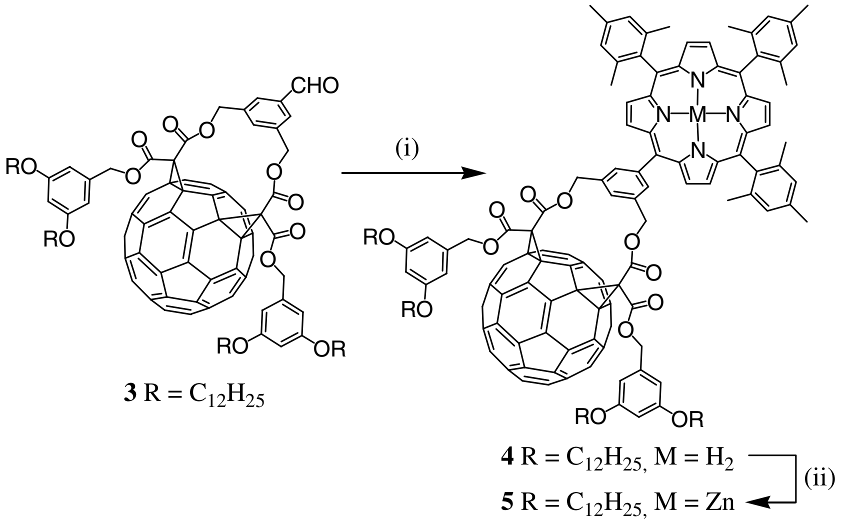


Figure 1. Compounds **1** and **2**.



3 R = $C_{12}H_{25}$

Scheme 1. Reagents and conditions: (i) mesitaldehyde, pyrrole, $BF_3{\cdot}Et_2O$, $CHCl_3$ (containing 0.75% EtOH), rt then *p*-chloranil, Δ (11%); (ii) $Zn(OAc)_2{\cdot}2H_2O$, $CHCl_3$/MeOH (9:1), Δ (84%).

rotation was estimated as $\Delta G^{\ddagger} = 18\ \text{kcal mol}^{-1}$ by following the coalescence of the aromatic mesityl protons H_a and $H_{a'}$.

The synthesis of compound **2** is depicted in Scheme 2. Compound **6**[7] and dipyrromethane **7**[8] were prepared according to previously reported methods. Condensation of **3** (1 equiv), **6** (1 equiv) and **7** (2 equiv) in $CHCl_3$ at room temperature in the presence of $BF_3{\cdot}Et_2O$ followed by *p*-chloranil oxidation and subsequent treatment with CF_3CO_2H in CH_2Cl_2 gave porphyrin **7** in an overall 4.5% yield. This low yield is explained by partial cleavage of the acetal protecting group under the acidic conditions used for the condensation reaction.

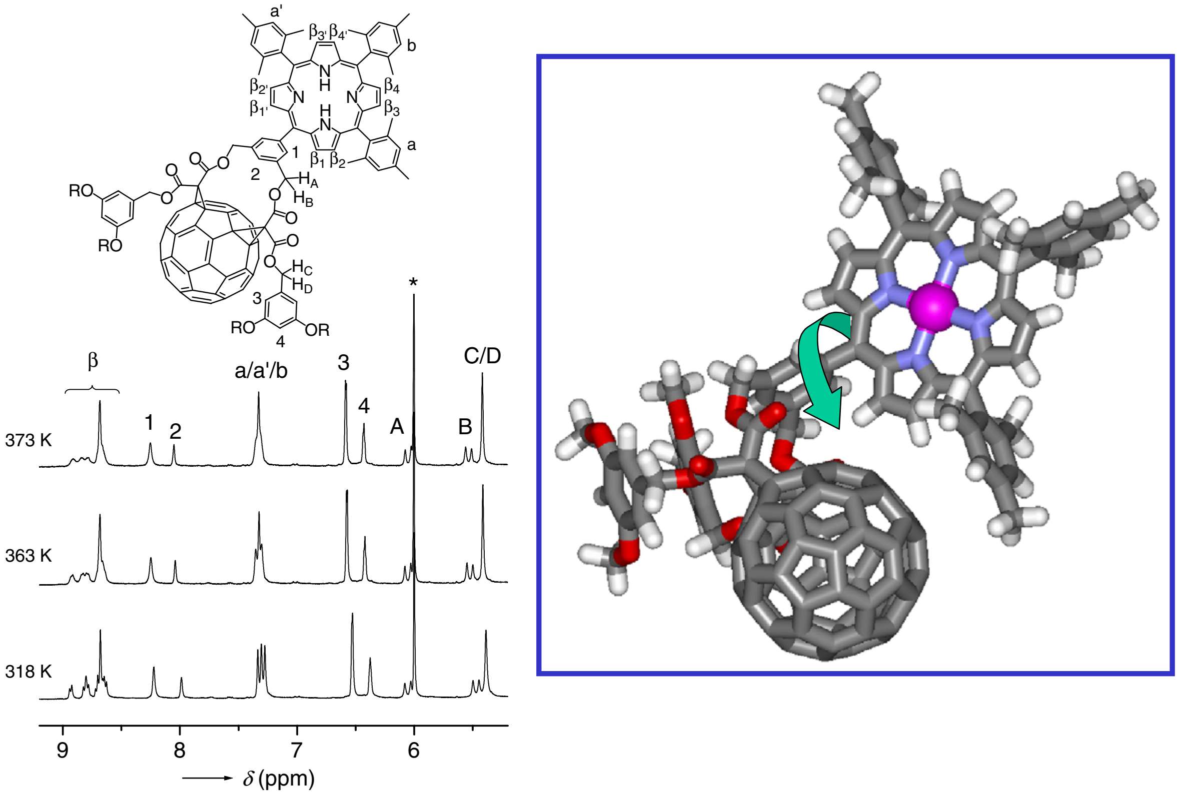
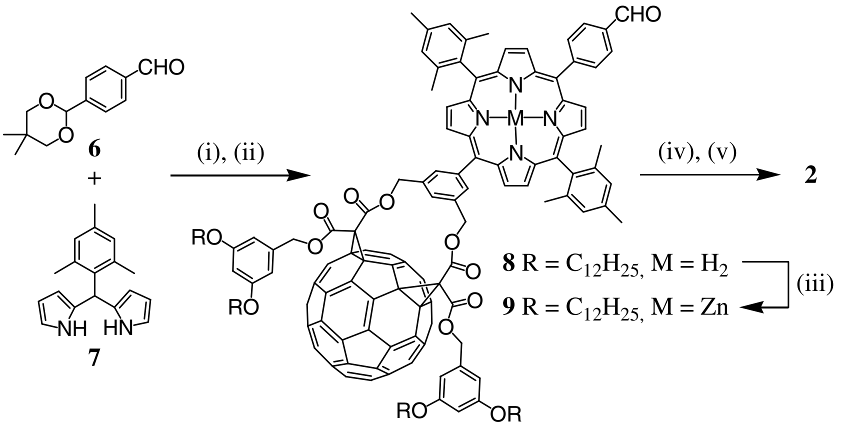


Figure 2. Right: calculated structure of **5** (the dodecyl chains have been replaced by methyl groups in the calculations). Left: ^{1}H NMR spectra (250 MHz) of **4** recorded in $CDCl_2CDCl_2$ at different temperatures (* = solvent peak).



Scheme 2. Reagents and conditions: (i) **3**, $BF_3{\cdot}Et_2O$, $CHCl_3$ (containing 0.75% EtOH), rt then *p*-chloranil, Δ (5%); (ii) CF_3CO_2H, CH_2Cl_2, rt (90%); (iii) $Zn(OAc)_2{\cdot}2H_2O$, $CHCl_3$/MeOH (9:1), Δ (87%); (iv) pyrrole, $BF_3{\cdot}Et_2O$, $CHCl_3$ (containing 0.75% EtOH), rt then *p*-chloranil, Δ (57%); (v) $Zn(OAc)_2{\cdot}2H_2O$, $CHCl_3$/MeOH (9:1), Δ (82%).

Metalation of porphyrin **8** with $Zn(OAc)_2$ gave **9** in 87% yield. Subsequent condensation of aldehyde **9** with pyrrole in $CHCl_3$ with $BF_3{\cdot}Et_2O$ as the catalyst followed by *p*-chloranil oxidation yielded porphyrin **1**, which was metalated with $Zn(OAc)_2$ to give **2**. The structure of both **1** and **2** was confirmed by MALDI-TOF mass spectrometry. The expected molecular ion peaks were observed at *m*/*z* 10816.1 for **1** ($[M]^+$, calcd for $C_{740}H_{614}N_{20}O_{48}Zn_4$: 10815.35 (100%), 10816.36 (93.5%), 10814.36 (87.3%)) and *m*/*z* 10878.1 for **2** ($[M]^+$, calcd for $C_{740}H_{612}N_{20}O_{48}Zn_5$: 10879.27 (100%), 10879.26 (97.9%), 10877.27 (97.9%)).

The characterization of **1** and **2** was complicated since these compounds appeared as mixtures of conformers in slow equilibrium on the NMR time scale at room temperature. As shown in Figure 3 for compound **2**, the ^{1}H NMR spectrum recorded at room temperature is quite broad. Indeed, each of the terminal fullerene substituent can be located either on one or on the other

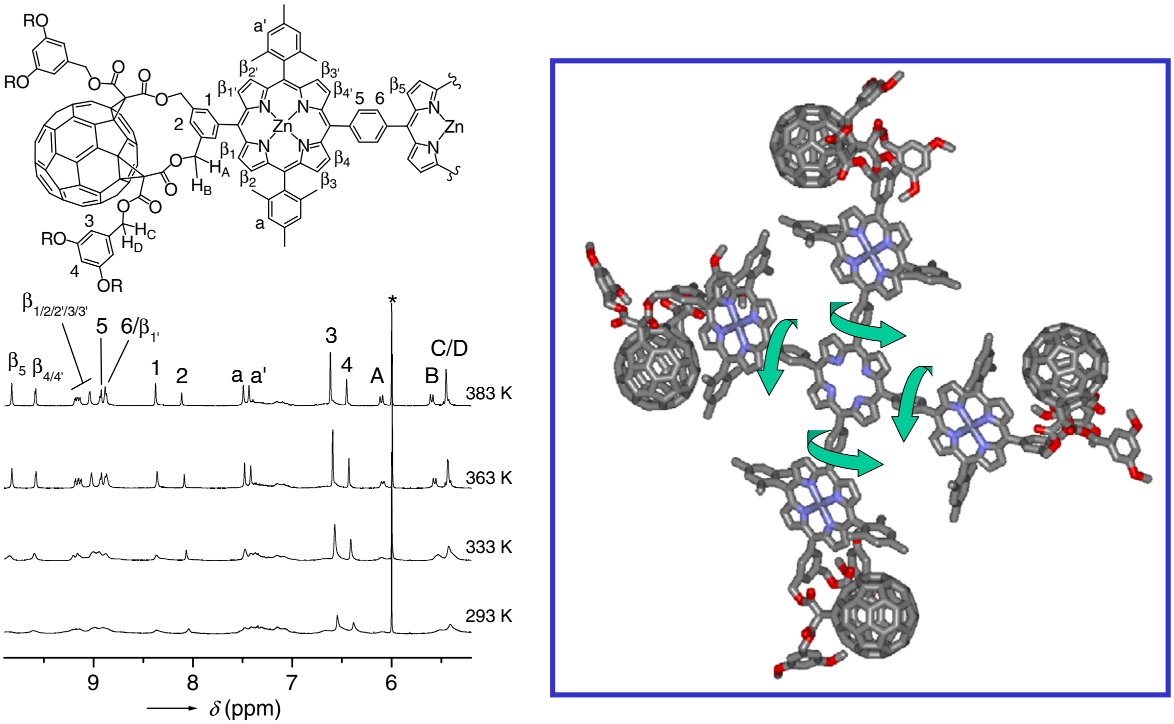


Figure 3. Right: calculated structure of **1** (the dodecyl chains have been replaced by methyl groups in the calculations). Left: ^1H NMR spectra (500 MHz) of **2** recorded in $CDCl_2CDCl_2$ at different temperatures (* = solvent peak).

side of its bridging phenyl group. Free rotation of the four substituents on the central porphyrin is therefore required to obtain a sharp symmetric NMR spectrum. Variable-temperature studies ($C_2D_2Cl_4$, 500 MHz) showed a perfectly reversible narrowing of all the peaks and a sharp spectrum was obtained at 383 K for both **1** and **2**. At this temperature, the dynamic exchange between the different atropisomers is fast on the NMR timescale, thus leading to a well resolved average spectrum. As shown in Figure 2, the spectrum of **2** recorded at 383 K is characterized by the diagnostic signals arising from the 1,3-phenylenebis(methylene)-tethered fullerene cis-2 bis-adduct substituent. Effectively, an AB quartet and a singlet are observed for the diastereotopic benzylic CH_2 groups ($H_{A–B}$ and $H_{C–D}$) and an AX_2 system is revealed for the aromatic protons of the 1,3,5-trisubstituted bridging phenyl ring (H_1 and H_2). The spectrum is also characterized by a singlet at δ 9.82 ppm for the 8 equiv β-pyrrolic protons of the central porphyrin core. Close inspection of the signals arising from the β-pyrrolic protons of the 4 equiv peripheral porphyrin subunits suggests restricted rotation of the 3,5-substituted phenyl substituent on those porphyrin rings under these conditions ($C_2D_2Cl_4$, 383 K, 500 MHz). This is further confirmed by the non-equivalence of their two mesityl substituents. Effectively, two singlets are seen for the mesityl protons H_a and $H_{a'}$ as in the cases of the spectra of model compounds **4** and **5** recorded at 318 K ($C_2D_2Cl_4$, 250 MHz). Therefore, rotation of the 3,5-substituted phenyl substituent on the peripheral porphyrin ring is still not fast enough on the NMR timescale to explain the obtention of a sharp symmetric spectrum for **1** and **2** at high temperature. Actually, for both **1** and **2**, the dynamic exchange between the different atropisomers is an unambiguous signature of the restricted rotation of the *para*-substituted phenyl substituents on the central porphyrin ring.

The UV/vis spectra of CH_2Cl_2 solutions of **2** and **5** are shown in Figure 4. The absorption spectrum of **5** shows the characteristic Zn(II)–porphyrin absorptions.[9] The Soret band (421 nm) and the two Q bands (549 and 570 nm) are clearly visible. Furthermore, the characteristic fullerene cis-2 bis-adduct absorption profile[10] is also distinguishable in the UV region and the absorption coefficients are consistent with a 1:1 fullerene to porphyrin ratio. Interestingly, the UV/vis spectrum of **2** shows

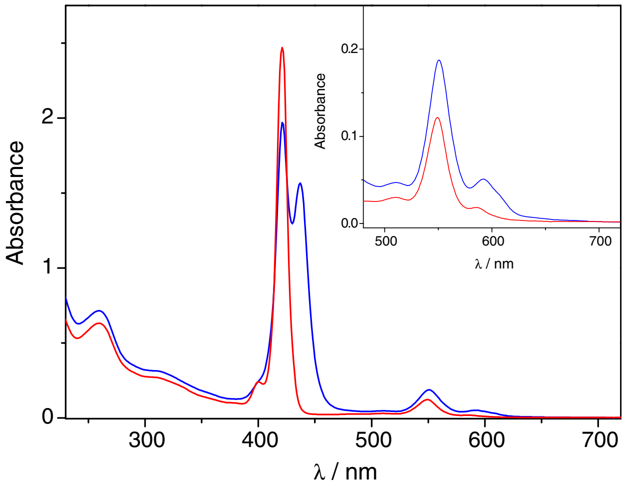


Figure 4. Absorption spectra of CH_2Cl_2 solutions of **5** (red) and **2** (blue).

a splitting of the Soret band as well as a slight red shift for the Q bands. The latter observation is a clear signature of exciton and electronic couplings between the various porphyrin units in compound **2**.[11] Finally, preliminary luminescence measurements reveal no emission from the porphyrin moieties in **2** or **5** indicating a strong quenching of their fluorescence by the fullerene subunits and thus, the occurrence of intramolecular photo-induced processes. Detailed photophysical studies are currently under investigation and special emphasis is placed on the detection of long-lived charge-separated states.

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