Dynamic *cis*/*trans* isomerisation in a porphyrin–fullerene conjugate

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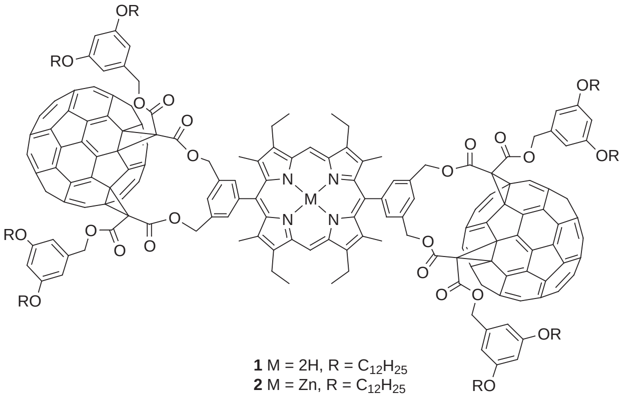
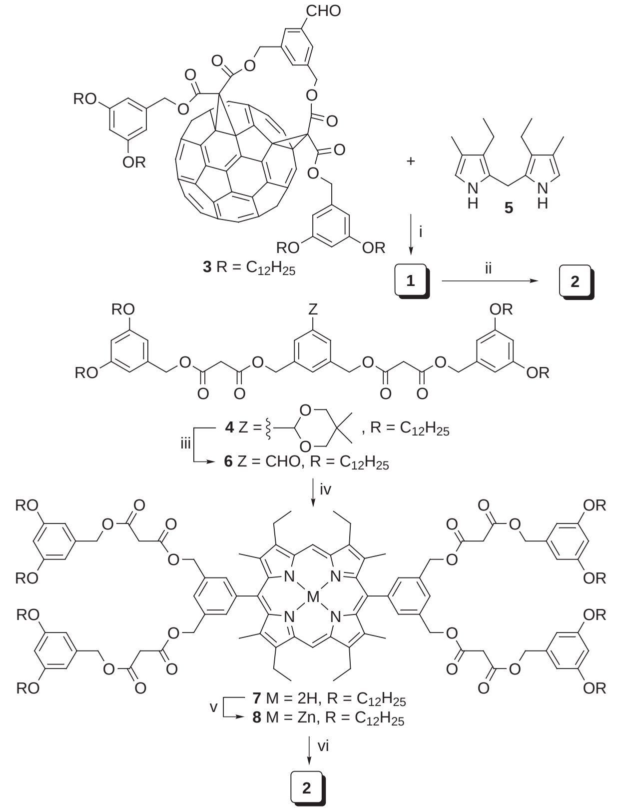
A porphyrin with two fullerene substituents is prepared by condensation of a C_{60} aldehyde derivative and dipyrrol-2-yl methane and by reaction of a preconstructed porphyrin with C_{60} itself; it is obtained as a mixture of two conformers in slow equilibrium, as shown by a variable temperature NMR study.

Since the first reported preparation of a C_{60}-linked porphyrin by Gust,[1] several other fullerene–porphyrin hybrids have been described.[2] Intramolecular processes such as electron and energy transfer have been observed in some of these compounds and C_{60} appears as a particularly interesting electron acceptor in photochemical molecular devices because of its symmetrical shape, large size and the properties of its π-electron system.[3] Concerning their synthesis, all the previously reported porphyrin–C_{60} hybrids have been prepared by reaction of a preconstructed porphyrin with C_{60} itself or a C_{60} acid derivative.[2] We have recently shown that a porphyrin could be constructed starting from a C_{60} aldehyde derivative and pyrrole.[4] As a part of this research, we now report the synthesis of the novel porphyrin **1** with two C_{60} groups directly attached to the core using our methodology. Furthermore, the corresponding Zn^{II}–porphyrin **2** has been prepared by metalation of **1**, but also by reaction of a preconstructed Zn^{II}–porphyrin with C_{60} itself. Interestingly, both **1** and **2** have been obtained as a mixture of two conformers and an NMR study reveals a previously unreported type of dynamic *cis*/*trans* isomerisation.

The synthesis of porphyrin **1** and its Zn^{II} complex **2** is depicted in Scheme 1. Aldehyde **3**,[4] compound **4**[4] and dipyrrol-2-yl methane **5**[5] were prepared according to previously reported methods. The condensation of **3** and **5** was performed in $CHCl_3$ at room temperature in the presence of $BF_3 \cdot Et_2O$. After 12 h, *p*-chloranil was added to irreversibly convert the porphyrinogen to the porphyrin. The desired porphyrin **1** was isolated in 38% yield and subsequent metalation with $Zn(OAc)_2$ gave **2** in 97% yield. Compound **2** could also be prepared starting from **4**: deprotection (TFA, CH_2Cl_2, H_2O), subsequent condensation of the resulting aldehyde **6** with **5** in $CHCl_3$ with $BF_3 \cdot Et_2O$ as catalyst and *p*-chloranil oxidation yielded porphyrin **7**, which was metalated with $Zn(OAc)_2$ to give **8**. Fullerene incorporation was based on the regioselective macrocyclisation reaction of the carbon sphere with bismalonate derivatives developed by Diederich and co-workers.[6] Treatment of C_{60} with **8**, I_2 and DBU in toluene at room temperature afforded a mixture of compounds from which the desired Zn^{II}–porphyrin **2** could be subsequently isolated in 2% yield by tedious chromatographic separations. This poor yield could be easily explained by a low selectivity of the intramolecular addition to C_{60} due to competition between the different available reactive malonic units on the porphyrin core after its first intermolecular reaction with C_{60}.



1 M = 2H, R = $C_{12}H_{25}$
2 M = Zn, R = $C_{12}H_{25}$



Scheme 1 *Reagents and conditions*: i, $CHCl_3$, $BF_3 \cdot Et_2O$, room temp., 12 h, then *p*-chloranil, reflux, 2 h, 38%; ii, $Zn(OAc)_2$, $CHCl_3$, MeOH, reflux, 2 h, 97%; iii, TFA, CH_2Cl_2, H_2O, room temp., 5 h, 80%; iv, **5**, $CHCl_3$, $BF_3 \cdot Et_2O$, room temp., 12 h, then *p*-chloranil, reflux, 2 h, 47%; v, $Zn(OAc)_2$, $CHCl_3$, MeOH, reflux, 3 h, 92%; vi, C_{60}, DBU, I_2, toluene, room temp., 12 h, 2%

All of the spectroscopic studies and elemental analysis results were consistent with the proposed molecular structures.‡ The ^1H NMR spectrum of **1** at room temperature showed the presence of two conformers in a 1 : 1 ratio (Fig. 1). Molecular modelling studies on compound **1** revealed that each fullerene group is located to one side of the plane of its bridging phenyl ring. Therefore due to the high barrier to rotation of the phenyl substituents on the porphyrin, two conformers are possible for **1**. The two carbon spheres in **1** can be in either a *cis* or *trans* relative orientation (Fig. 1). Whereas the two porphyrin *meso*-

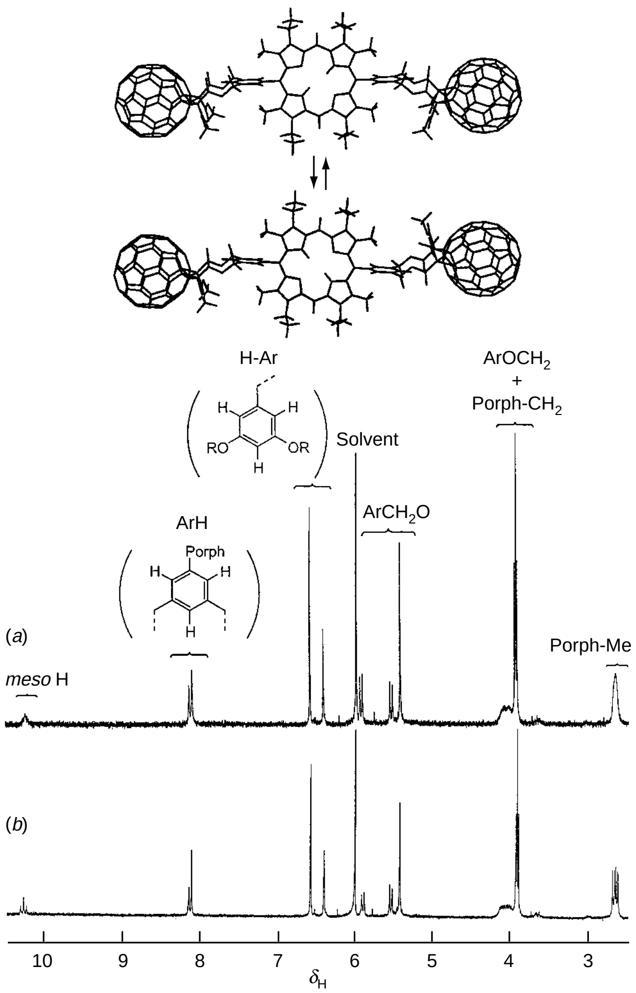


Fig. 1 ^{1}H NMR spectra of **1** ($CDCl_2CDCl_2$, 400 MHz) at (a) 125 and (*b*) 25 °C, and molecular models of the two conformers of compound **1** (the four didodecyloxyphenyl groups have been omitted for clarity)

Hs are equivalent in the *trans* conformer, they are non-equivalent in the *cis* one. As expected, three singlets in a 1 : 2 : 1 ratio are observed at δ 10.20, 10.23 and 10.27, respectively, for the *meso*-Hs in the 1 : 1 mixture of conformers. Furthermore, the four methyl groups on the porphyrin form equivalent pairs in both conformers and the expected four singlets are clearly observed (δ 2.60, 2.63, 2.64 and 2.67) in the ^{1}H NMR spectrum. A variable-temperature NMR study showed a clear coalescence at 125 °C (Fig. 1). By monitoring the coalescence of the porphyrin *meso*-Hs, the free energy barrier for the conformational equilibrium was calculated as $\Delta G^{\ddagger}$ = 85 kJ mol^{-1}.[7] A sharp symmetric spectrum could not be obtained below the limit of heating, however the observed reversible narrowing of all the peaks unambiguously shows that a dynamic effect does occur. This *cis*/*trans* isomerism has also been seen for compound **2** and can be related to the diastereoisomerism observed for some terphenyl systems.[8] Whereas atropisomerism in bis(*o*-substituted phenyl) porphyrins is well known, the conformational isomerism observed for **1** and **2** is, to the best of our knowledge, the first example of a bis(*m*-substituted phenyl) porphyrin for which the barrier to free rotation is high enough at room temperature to be able to distinguish the *cis* and *trans* conformers.

Preliminary luminescence measurements show a strong quenching of the porphyrin emission in **1** and **2** and their photophysical properties are currently under investigation.

We thank the CNRS for financial support, C. Bourgogne for his help with the molecular modelling, Hoechst AG for samples of C_{60} and Professor F. Diederich (Zürich, Swiss) for his interest in our work and his support.

Notes and References

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‡ *Selected data* for **1**: λ_{max}(CH_2Cl_2)/nm (ε/dm^3 mol^{-1} cm^{-1}) 259 (275 580), 317 (96 370), 382 (sh, 133 130), 408 (284 740), 506 (27 000), 539 (10 580), 573 (11 050), 624 (2680); ν_{max}($CHCl_3$)/cm^{-1} 1748 (C=O); *m/z* (ESI) 4360 (M$^+$) (Calc. for $C_{304}H_{270}N_4O_{24}$: C, 83.68; H, 6.24; N, 1.28. Found: C, 83.79; H, 6.29; N, 1.27%).

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Received in Cambridge, UK, 7th May 1998; 8/03434F