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A novel synthetic approach to 27-aryltetrabenzo[5,10,15]triazaporphyrins

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Magnesium 27-aryltetrabenzo[5,10,15]triazaporphyrinates were obtained by heating of phthalodinitrile, arylacetonitrile and magnesium powder.

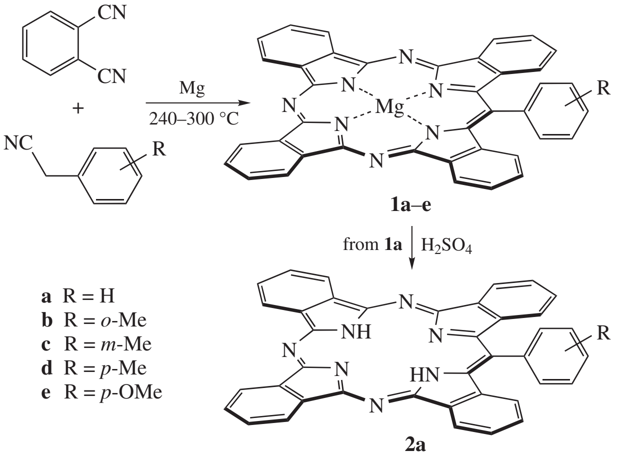
Tetrabenzo[5,10,15]triazaporphyrins are close analogues of phthalocyanines differing in the presence of a hydrocarbon bridge instead of the nitrogen atom in the *meso*-position. Although they are widely used as photoconductive materials,[1] fluorescent markers in medicine[2,3] and gas sensors,[4] the number of methods for their preparation is limited. It was recently reported[5] that 1,4,8,11,15,18,22,25-octahexyltetrabenzo[5,10,15]triazaporphyrin was isolated as a side product in the synthesis of 1,4,8,11,15,18,22,25-octahexylphthalocyanine by treatment of 3,6-dihexylphthalodinitrile with lithium pentoxide in *n*-pentanol, whereas no tetrabenzo[5,10,15]-triazaporphyrin derivatives but only substituted phthalocyanines were formed from 4,5-disubstituted phthalodinitriles.

A synthesis of copper tetrabenzo[5,10,15]triazaporphyrin by heating a mixture of phthalodinitrile, 3-methylenephthalimidine and copper chloride at 250 °C was first reported in 1938.[6] One of the general methods for synthesizing tetrabenzo[5,10,15]triazaporphyrins involves treatment of phthalodinitrile with organomanganese reagents followed by refluxing in a high-boiling solvent.[7,8] Studies on the synthesis of 27-phenyltetrabenzo[5,10,15]triazaporphyrins by reaction of 1,3-diiminoisoindoline with phenylacetic acid in the presence of template agents at 280 °C have been published recently.[9,10] However, these approaches are either unpractical as they involve several stages and anhydrous conditions,[8] or result in hardly separable mixtures of metal complexes.[10]

The low solubility of tetrabenzo[5,10,15]triazaporphyrin complicates its isolation in individual form because chromatographic purification cannot be used. The incorporation of a non-coplanar substituent at a *meso*-position of the macrocyclic system should increase the solubility of the target products and hence facilitate preparation of pure individual compounds.

Here we report on novel approach to 27-aryltetrabenzo-[5,10,15]triazaporphyrins by simple heating to 300 °C of phthalodinitrile accessible in industrial amounts with arylacetonitriles possessing reactive hydrogen atoms in the presence of magnesium metal. The primary products are the corresponding magnesium complexes **1** (Scheme 1).[†]

The target 27-aryltetrabenzo[5,10,15]triazaporphyrin complexes **1** were also prepared by microwave irradiation of the reactants. As we have shown previously, optimum yields of substituted phthalocyanines are reached by applying a microwave power of 650–700 W for 6–10 min.[11] To synthesise compound **1a**, a mixture of phthalodinitrile, phenylacetonitrile and magnesium powder was kept at 600 W for 8 min.[‡] It was found that the melt acquired a phthalocyanine colour in 2 min. Complete conversion of phthalodinitrile occurred in another 5 min. The yield (11%) was 2% higher than that in the fusion method.



Scheme 1

Owing to the high solubility of magnesium complexes of 27-aryltetrabenzo[5,10,15]triazaporphyrins in organic solvents, the products were separated by column chromatography. The synthesis resulted in dark-blue crystalline compounds soluble in most of common organic solvents (benzene, chloroform, acetone, dimethylsulfoxide) but insoluble in hexane and methanol. The electronic absorption (UV-VIS) spectra of the products are characterised by intense bands in the long-wave region (600–675 nm, Q-bands) and less intense bands in the short-wave region (350–450 nm,

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[†] *Synthesis of magnesium complexes* **1a**–**e** *(general procedure).* A flask equipped with a reflux condenser and an inert gas inlet and containing a mixture of phthalodinitrile (2.0 mmol), arylacetonitrile (0.5 mmol) and magnesium powder (0.5 mmol) was placed under argon in an oil bath heated to 190 °C. The resulting reddish-orange melt soon turned cyan and then was heated with a gradual temperature increase from 195–200 °C to 290–300 °C and kept for 2 h at that temperature. The resulting dark blue crystalline product was dissolved with heating in THF. The solution was filtered from the magnesium phthalocyanine admixture, then chromatographed on a column with silica gel using THF as the eluent. The cyan-colored fraction was chromatographed once again on silica gel (hexane–THF, 5:1). The solvent was removed *in vacuo* and the dark-blue precipitate was refluxed in methanol for 15 min. The product was filtered off and dried *in vacuo* at 140 °C.

For **1a**: yield 9%. UV-VIS [THF, $\lambda_{\max}$/nm ($I/I_{\max}$)]: 397 (0.437), 443 (0.195), 594 (0.174), 618 (0.176), 648 (0.674), 670 (1.000). ^{1}H NMR (DMSO-d_6) δ: 9.53 (d, 2H, β^2-H$_{\mathrm{Ar}}$, J 7.5 Hz), 9.43 (m, 4H, β^1-H$_{\mathrm{Ar}}$), 7.94–8.29 (m, 11H, γ^1-H$_{\mathrm{Ar}}$, γ^2-H$_{\mathrm{Ar}}$, H$_{\mathrm{Ph}}$), 7.66 (t, 2H, γ^3-H$_{\mathrm{Ar}}$, J 7.5 Hz), 6.98 (d, 2H, β^3-H$_{\mathrm{Ar}}$, J 8.1 Hz). MS (MALDI-TOF), m/z: 612 [M$^+$].

B-bands). The nature of the aryl substituent in the magnesium complex insignificantly affects the character of the spectra and the positions of the absorption band maxima. Figure 1 shows the UV-VIS of complex **1a** in tetrahydrofuran as an example.

The mass spectra (MALDI-TOF) of the complexes obtained exhibit molecular ion peaks which contain signals matching the isotopic composition of magnesium.

Complexes **1** were also characterised by ^{1}H and ^{13}C NMR spectroscopy. The signals in the spectra were assigned using two-dimensional (2D) techniques. Figure 2 presents a ^{1}H–^{1}H COSY spectrum of complex **1c** having characteristic cross-peaks as an example. A specific feature of the spectrum is that the signals of α^3-H protons are shifted upfield by 2.39 ppm with respect to those of α^1-H protons; this effect is because the former are located in the shielding cone of the aryl substituent arranged orthogonally to the macrocycle plane. A similar effect, albeit not so pronounced, is also observed for the β^3-H$_{\mathrm{Ar}}$ and β^2-H$_{\mathrm{Ar}}$ protons, which are shielded by 0.58 and 0.32 ppm, respectively, relative to β^1-H$_{\mathrm{Ar}}$. Conversely, in the case of α^2-H protons, weak deshielding of signals by 0.09 ppm with respect to α^1-H is observed, which suggests that weakening of the magnetic effect of the *meso*-aryl group occurs. The signals of carbon atoms in the ^{13}C NMR spectrum of **1c** were assigned using ^{1}H–^{13}C COSY and DEPT-135 techniques, as well as the scarce literature data.[5] Note that the methine carbon atom in **1c** is deshielded (δ 125.88) with respect to the *meso*-unsubstituted analogue,[5] which displays the corresponding signal at δ 104.6.

The magnesium complexes **1** can be readily demetallated to give free 27-aryl-29*H*,31*H*-tetrabenzo[5,10,15]triazaporphyrins **2**. In fact, treatment of compound **1a** with concentrated sulfuric acid gave the respective ligand **2a** in a quantitative yield;[§] it was characterised by MALDI-TOF mass spectrometry (see Online Supplementary Materials, Figure 1S) and UV-VIS spectroscopy (Figure 1). The electronic spectrum of this ligand, similarly to that of compounds **1** with $C_{2\mathrm{v}}$ symmetry, is also characterised by a split Q-band. It is evident from Figure 1 that demetallation increases the degree of this splitting: the Q$_1$ component is shifted hypsochromically by 5 nm, whereas the Q$_2$ band shows a bathochromic shift of 15 nm.

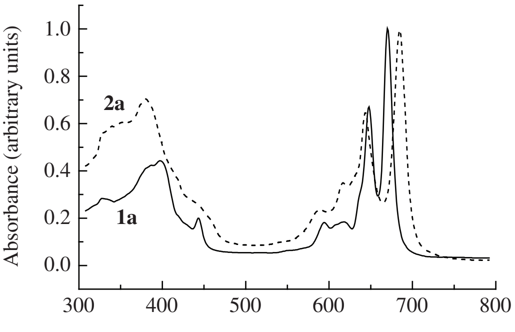

Figure 1 Electronic absorption spectra of magnesium complex **1a** and the corresponding free-base ligand **2a** in THF.

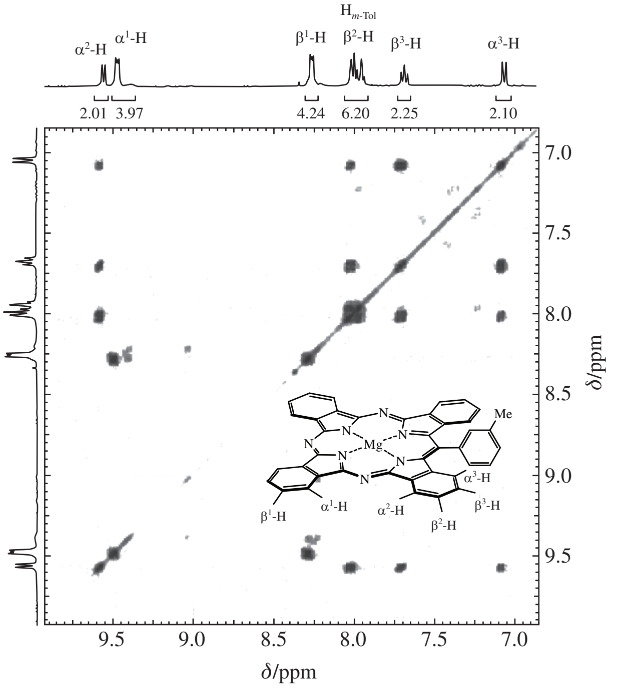

Figure 2 ^{1}H–^{1}H COSY NMR spectrum of compound **1c** (aromatic region) in DMSO-d_6.

The ligand **2** has been proved to be promising in syntheses of sandwich rare-earth metal complexes that represent a new type of complexes of these elements.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2011.03.011.

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For **1c**: yield 10%. UV-VIS [THF, λ_{max}/nm (I/I_{max})]: 397 (0.432), 444 (0.180), 594 (0.173), 619 (0.187), 648 (0.653), 670 (1.000). ^{1}H NMR (DMSO-d_6) δ: 9.53 (d, 2H, β^2-H$_{\mathrm{Ar}}$, *J* 7.5 Hz), 9.43–9.45 (m, 4H, β^1-H$_{\mathrm{Ar}}$), 8.23–8.26 (m, 4H, γ^1-H$_{\mathrm{Ar}}$), 7.93–7.99 (m, 6H, γ^2-H$_{\mathrm{Ar}}$, H$_{m\text{-Tol}}$), 7.67 (t, 2H, γ^3-H$_{\mathrm{Ar}}$, *J* 7.5 Hz), 7.05 (d, 2H, β^3-H$_{\mathrm{Ar}}$, *J* 8.1 Hz), 2.65 (s, 3H, H$_{\mathrm{Me}}$). ^{13}C NMR (DMSO-d_6) δ: 155.32, 152.30, 151.16, 138.63 (C-5, C-7, C-12, C-14, C-19, C-21, C-26, C-28), 141.73, 141.64 (C$_{m\text{-Tol}}$-1, C$_{m\text{-Tol}}$-3), 139.35, 139.06, 138.85, 138.22 (C-4a, C-7a, C-11a, C-14a, C-18a, C-21a, C-25a, C-28a), 132.24, 130.02, 129.10, 128.76 (C$_{m\text{-Tol}}$-2, C$_{m\text{-Tol}}$-4, C$_{m\text{-Tol}}$-5, C$_{m\text{-Tol}}$-6), 129.72, 129.42 (C-9, C-10, C-16, C-17), 127.64 (C-2, C-24), 126.92 (C-3, C-23), 125.88 (C-27), 124.30 (C-1, C-25), 122.74, 122.54, 122.45 (C-4, C-8, C-11, C-15, C-18, C-22), 21.25 (C–Me). MS (MALDI-TOF), *m*/*z*: 626 [M$^+$].

For characteristics of complexes **1b**,**d**,**e**, see Online Supplementary Materials.

[‡] A mixture of phthalodinitrile (0.77 g), phenylacetonitrile (0.18 g) and magnesium powder (0.11 g) was irradiated at 600 W for 8 min in a Samsung M1915NR microwave oven to afford compound **1a**, yield 11%.

[§] *27-Phenyl-29*H*,31*H*-tetrabenzo[*b,g,l,q*][5,10,15]triazaporphyrin* **2a**. The magnesium complex **1a** (10 mg, 0.016 mmol) was dissolved in concentrated H$_2$SO$_4$ and kept for 1 min, then poured onto ice. The precipitate was filtered off, washed consecutively with H$_2$O to neutral pH and 80% aqueous MeOH (3×20 ml) and finally dried *in vacuo*. Yield 98%. UV-VIS [THF, λ_{max}/nm (I/I_{max})]: 380 (0.719), 590 (0.257), 617 (0.369), 643 (0.658), 685 (1.000). MS (MALDI-TOF), *m*/*z*: 589 [M$^+$].