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# Design and Synthesis of Porphyrins Bearing Catechols

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**Abstract:** The synthesis of *meso*-tetraarylporphyrines bearing 1-4 catechoylamid groups was achieved. Among the four new compounds prepared, the structure of the disubstituted ligand was elucidated in the solid state by an X-ray analysis. © 1997 Elsevier Science Ltd.

Over the past three decades, the design and synthesis of binuclear complexes have been extensively studied.[1] Recently, we have embarked upon a program dealing with the design and the synthesis of polynucleating ligands. Using preorganised cores, such as [22]diaza macrocycle[2] and calix[4]arene[3], bi- and poly-nucleating ligands bearing bidentate catechol units have been prepared. The bidentate bipyridine ligand has been also incorporated within macrocyclic frameworks.[4] Binucleating ligands based on mercaptocalix[4]arenes have been also reported.[5] Our approach to the design of new bi- and poly-nucleating ligands was based on the combination of a porphyrin core and bidentate catechol moieties. Porphyrins present two major advantages. In addition to their ability to bind metal cations, they may also serve as a preorganised macrocyclic structure offering the possiblity of anchoring, at least, upto four lateral coordinating ligands. The bidentate catechol derivatives, on the other hand, have been shown to bind a wide variety of metal cations. The linkage of the latter to the porphyrin core may be achieved, either by direct fonctionalization of the porphyrin at the *meso* positions, or by using a spacer such as the phenyl group attached at the *meso* positions.

Porphyrins bearing bidentate ligands such as bipyridine[6] and phenantroline[7] have been reported. On the other hand, diaza-, triaza- and tetraaza-macrocycles bearing two, three and four pendant catecholate units respectively have been also previously reported.[8] To our knowledge, no examples of porphyrins bearing catechol moieties have been published so far. We report here the first synthesis of four new tetraarylporphyrins bearing 1-4 bidentate catechol units.

It has been well established that functionalisation of *meso*-tetraphenylporphyrins at the *ortho* position on the phenyl rings leads to atropoisomers.[9] In order to avoid this, the connection of the catechol units was achieved at the *meta* position (**16**, **18**, **20**, **22**). For the mono- (**16**), di- (**18**) and tri- (**20**) catechol substitued porphyrins, the remaining *meso* positions, for solubility reasons, were functionalised with tolyl groups. Dealing with the junction between the porphyrin and the bidentate ligand, since catecholamine is known to be less stable towards oxidation than catecholamide, our design was based on the latter functionality.

Although the synthesis of a variety of *meso*-tetraarylporphyrines bearing amino groups at the *ortho* and the

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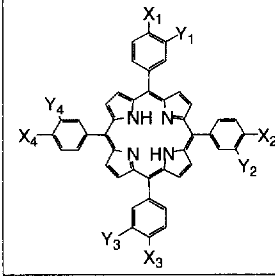
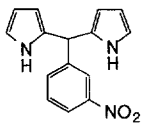
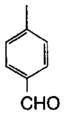
*para* positions has been extensively studied, for *meso*-tetraarrylporphyrins bearing amino group at *meta* positions of the peripheral phenyl groups, only few examples have been reported.[10]



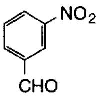
**1** $X_1 = H$; $X_i = CH_3$ (i = 2-4); $Y_1 = NO_2$; $Y_i = H$ (i = 2-4)
**2** $X_1 = X_2 = H$; $X_i = CH_3$ (i = 3-4); $Y_1 = Y_2 = NO_2$; $Y_i = H$ (i = 3-4)
**3** $X_1 = X_3 = H$; $X_i = CH_3$ (i = 2,4); $Y_1 = Y_3 = NO_2$; $Y_i = H$ (i = 2,4)
**4** $X_i = H$ (i = 1-3); $X_4 = CH_3$; $Y_i = NO_2$ (i = 1-3); $Y_4 = H$
**5** $X_i = H$ (i = 1-4); $Y_i = NO_2$ (i = 1-4)
**6** $X_1 = H$; $X_i = CH_3$ (i = 2-4); $Y_1 = NH_2$; $Y_i = H$ (i = 2-4)
**7** $X_1 = X_2 = H$; $X_i = CH_3$ (i = 3-4); $Y_1 = Y_2 = NH_2$; $Y_i = H$ (i = 3-4)
**8** $X_1 = X_3 = H$; $X_i = CH_3$ (i = 2,4); $Y_1 = Y_3 = NH_2$; $Y_i = H$ (i = 2,4)
**9** $X_i = H$ (i = 1-3); $X_4 = CH_3$; $Y_i = NH_2$ (i = 1-3); $Y_4 = H$
**10** $X_i = H$ (i = 1-4); $Y_i = NH_2$ (i = 1-4)



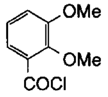
**11**



**12**



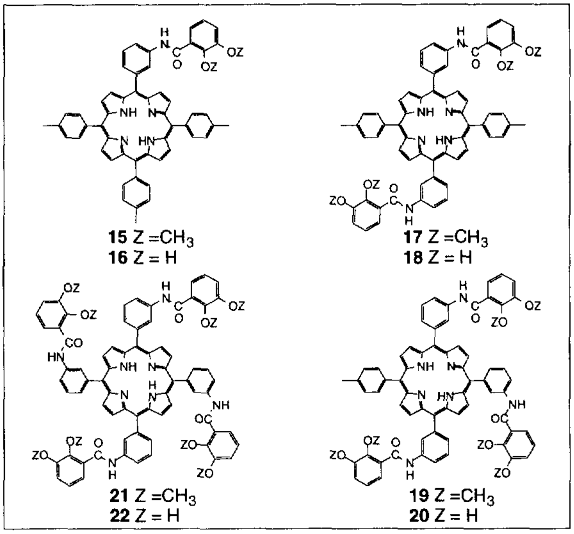
**13**



**14**

The mono- (**6**), di- (**7**, **8**), tri- (**9**) and tetra-aminoporphyrins **10** were obtained upon reduction by $SnCl_2$/HCl of the corresponding nitrophenylporphyrins **1-5**. The latter compounds were obtained, using different synthetic strategies, by condensation of pyrrole with either benzaldehyde derivatives (**12**, **13**) or with the *meso*-prefunctionalised dipyrrylmethane derivative **11**. It is worth noting that due to the deactivating effect of the nitro group on the reactivity of *m*-nitrobenzaldehyde, the yield for *meso*-tetraarylporphyrins bearing nitro groups at *meta* positions is usually low. The mononitroporphyrin **1** was prepared by the condensation of pyrrole with **12** and *m*-nitrobenzaldehyde **13** in $CHCl_3$ in the presence of $Et_2O$-$BF_3$ followed by treatment with DDQ. In order to increase the yield of **1** (8 %), a 4/2.5/1.5 ratio for pyrrole/**12**/**13** was used. Under these conditions, in addition to the desired compound **1**, *meso*-tetratolylporphyrin (5 %) as well as dinitro compounds **2** and **3** (6 % overall) and trinitro compound **4** (3 %) were isolated by column chromatography on silica. Although compound **3** was formed under the above mentioned conditions, in order to increase its yield a more directed strategy was employed. Upon condensation of the dipyrrylmethane **11**, prepared by treatment of *m*-nitrobenzaldehyde **13** with neat pyrrole, with **12** in $CHCl_3$ in the presence of $Et_2O$-$BF_3$ followed by oxidation with DDQ, in addition to the *meso*-tetratolylporphyrin (1 %), compounds **1** (1 %), **2** and **3** (15 % overall) and the trinitroporphyrin **4** (1.4 %) were isolated. The formation of *meso*-tetratolylporphyrin, compounds **1**, **4**, as well as the other dinitro regioisomer **2** were due to acid-catalyzed redistribution reactions as previously reported for other tetraarylporphyrins.[11] Finaly, the tetranitroporphyrin **5** was prepared upon condensation of pyrrole with **13** in a 1/1 ratio following the reported procedure.[12] The aminoporphyrin **6** was obtained in 45 % yield upon reduction by $SnCl_2$-$2H_2O$/conc. HCl in THF at 80 °C. Dealing with the desired diaminoporphyrin **8**, since the separation between the two regioisomers **2** and **3** was found to be rather tedious at the nitro level, the mixture was first reduced by $SnCl_2$-$2H_2O$/conc.HCl at 80 °C affording a mixture of **7** and **8** in 59 % overall yield. At that stage, the separation appeared to be less tedious and both compounds **7** (16 %) and **8** (43 %) were purified by column chromatography ($SiO_2$). The triaminoporphyrin **9** (34 %) was obtained by treatment of **4** with $SnCl_2$-$2H_2O$/conc.HCl at 80 °C. Finally, the tetraminoporphyrin **10** was prepared, following the reported procedure[12], by reaction with $SnCl_2$-$2H_2O$/conc.HCl at 80 °C.

The synthetic strategy for the preparation of **16**, **18**, **20** and **22** was based on the coupling of the acyl chloride derivative of the protected catechol **14**, prepared from the commercially available 2,3-dimethoxybenzoic acid by treatment with $SOCl_2$[13], with the amino porphyrins **7-10** followed by deprotection of the catechol groups using $BBr_3$.[14] The coupling reaction in all four cases was almost quantitative. The protected compounds **15**[15] (67 %), **17**[15] (67 %), **19**[15] (84 %) and **21**[15] (34 %) were obtained, after chromatography ($SiO_2$), upon condensation at r.t. of the aminoporphyrins with **14** in THF and in the presence of $Et_3N$. The rather low yield in the case of compound **21** was due to low solubility. The final compounds **16**[16] (76 %), **18**[16] (48 %), **20**[16] (62 %) and **22**[16] (30 %) were isolated after deprotection with $BBr_3/CH_2Cl_2$ at r.t. The final four compouds **16**, **18**, **20** and **22**, in addition to one dimensional $^1H$ and $^{13}C$ NMR spectroscopy, were characterised by two-dimensional $^1H$-$^{13}C$ NMR studies. Furthermore, they were characterised by high resolution mass spectrometry. Among the four functionalised porphyrins prepared, the solid state structure of compound **17** was also elucidated by an X-ray study (Fig.1).[17] The molecule was centrosymmetric. The porphyrin core of the ligand was almost planar. The tolyl and *m*-aminophenyl groups were tilted by 62.9° and 65.4° respectively with respect to the main plane of the porphyrin. The amide junctions were in trans configuration.



**15** Z =$CH_3$
**16** Z = H

**17** Z =$CH_3$
**18** Z = H

**21** Z =$CH_3$
**22** Z = H

**19** Z =$CH_3$
**20** Z = H

In summary, the synthesis of porphyrins bearing **1-4** bidentate catechol groups was achieved. An X-ray analysis for the difunctionalised ligand confirmed the data obtained by one- and two-dimensional NMR and mass spectrometry. The formation of the bi- and poly-nuclear complexes using the reported compounds with a variety of transition metal cations is under current investigation.

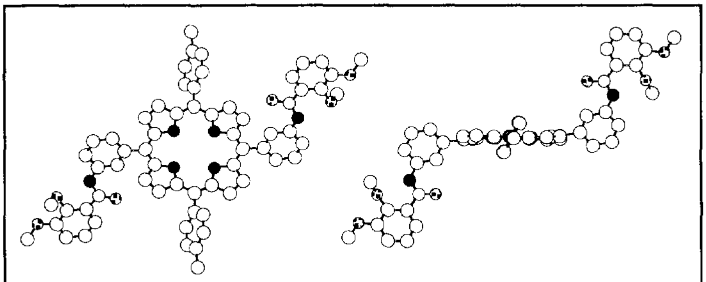


**Figure 1** : X-ray structure of **17**. Top (left) and lateral (right) views. For the sake of clarity, hydrogen atoms as well as solvent molecules are not presented.

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15. **15: $^{1}$H:** (CDCl$_3$, 300 MHz): -2.75 (s, 2H, NH pyr); 2.70 (s, 9H, CH$_3$); 3.89 (s, 3H, OCH$_3$); 3.99 (s, 3H, OCH$_3$); 7.08 (dd, 1H, J=8.1 Hz, J=1.6 Hz, Ar cat); 7.21 (t, 1H, J=8.1 Hz, Ar cat); 7.55 (d, 6H, J=7.7 Hz, Ar tol); 7.76 (t, 1H, J=7.7 Hz, Ar Ph); 7.84 (dd, 1H, J=8.1 Hz, J=1.8 Hz, Ar cat); 7.99 (ddd, 1H, J=7.7 Hz, J=1.5 Hz, J=1.1 Hz, Ar Ph); 8.10 (d, 6 H, J=8.1 Hz, Ar tol); 8.32 (ddd, 1H, J=8.5 Hz, J=1.1 Hz, J=0.7 Hz, Ar Ph); 8.38 (t, 1H, J=1.7 Hz, Ar Ph); 8.86 (d+s, 6H, H βpyr); 8.92 (d, 2H, J=4.8 Hz, H βpyr); 10.33 (s, 1H, NH); **$^{13}$C:** (CDCl$_3$, 75.4 MHz): 21.52, 56.13, 61.67, 115.85, 119.21, 119.68, 120.25, 120.38, 123.06, 124.66, 126.46, 126.73, 127.42, 130.92, 134.55, 136.94, 137.34, 139.29, 143.16, 147.35, 152.55, 163.48; **17: $^{1}$H:** (CDCl$_3$, 300 MHz): -2.74 (s, 2H, NH pyr); 2.70 (s, 6H, CH$_3$); 3.89 (s, 6H, OCH$_3$); 3.99 (s, 6H, OCH$_3$); 7.09 (dd, 2H, J=8.2 Hz, J=1.6 Hz, Ar cat); 7.21 (t, 2H, J=8.1 Hz, Ar cat); 7.55 (d, 4H, J=7.7 Hz, Ar tol); 7.75 (t, 2H, J=7.9 Hz, Ar Ph); 7.84 (dd, 2H, J=7.9 Hz, J=1.7 Hz, Ar cat); 8.01 (d, 2H, J=1.7 Hz, Ar Ph); 8.11 (d, 4H, J=7.9 Hz, Ar tol); 8.31 (d, 2H, J=8.1 Hz, Ar Ph); 8.38 (s, 2H, Ar Ph); 8.87 (d, 4H, J=4.8 Hz, H βpyr); 8.92 (d, 4H, J=4.8 Hz, H βpyr); 10.31 (s, 2H, NH); $^{13}$C : (CDCl$_3$, 75.4 MHz): 21.52, 56.16, 61.69, 116.00, 119.39, 119.71, 120.36, 123.15, 124.69, 126.46, 126.83, 127.38, 127.43, 130.89, 134.57, 136.94, 137.37, 139.27, 143.13, 147.46, 152.65, 163.48; **19: $^{1}$H:** (CDCl$_3$, 300 MHz): -2.74 (s, 2H, NH pyr); 2.70 (s, 3H, CH$_3$); 3.87 (s, 9H, OCH$_3$); 3.99 (s, 9H, OCH$_3$); 7.08 (d, 3H, J=8.0 Hz, Ar cat); 7.20 (t, 3H, J=8.0 Hz, Ar cat); 7.56 (d, 2H, J=7.9 Hz, Ar tol); 7.75 (t, 3H, J=7.7 Hz, Ar Ph); 7.84 (dd, 3H, J=7.9 Hz, J=1.4 Hz, Ar cat); 8.01 (d, 3H, J=7.3 Hz, Ar Ph); 8.11 (d, 2H, J=7.8 Hz, Ar tol); 8.30 (d, 3H, J=8.0 Hz, Ar Ph); 8.38 (s, 3H, Ar Ph); 8.87 (d, 2H, J=4.8 Hz, H βpyr); 8.92 (d+s, 6H, H βpyr); 10.32 (s, 3H, NH); $^{13}$C: (CDCl$_3$, 75.4 MHz): 21.52, 56.16, 61.72, 116.00, 119.46, 119.50, 119.74, 120.59, 123.17, 124.68, 126.45, 126.86, 127.44, 130.95, 134.58, 136.95, 137.40, 139.25, 143.08, 147.47, 152.66, 163.45; **21: $^{1}$H:** (CDCl$_3$, 300 MHz): -2.74 (s, 2H, NH pyr); 3.87 (s, 12H, OCH$_3$); 3.99 (s, 12H, OCH$_3$); 7.08 (d, 4H, J=7.1 Hz, Ar cat); 7.21 (t, 4H, J=8.1 Hz, Ar cat); 7.76 (t, 4H, J=7.7 Hz, Ar Ph); 7.84 (dd, 4H, J=8.0 Hz, J=1.5 Hz, Ar cat); 7.99 (d, 4H, J=7.4 Hz, Ar Ph); 8.32 (d, 4H, J=5.8 Hz, Ar Ph); 8.37 (s, 4H, Ar Ph); 8.95 (s, 8H, H βpyr); 10.32 (s, 4H, NH); $^{13}$C: (CDCl$_3$, 75.4 MHz): 56.12, 61.73, 115.94, 119.61, 119.75, 123.12, 126.26, 126.79, 127.42, 130.94, 136.92, 142.98, 147.47, 152.62, 163.47.
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17. *X-ray data for compound 17*: $C_{64}H_{52}N_6O_6$,2CHCl$_3$, *M* = 1239.92, monoclinic, *a* = 18.646(6), *b* = 7.129(3), *c* = 22.780(7) Å, β = 98.59(2)°, *U* = 2994(3) Å$^3$, space group P 1 21/c 1, Z = 2, *Dc* = 1.38 gcm$^{-3}$, μ(Cu-*K*α) = 3.134 mm$^{-1}$. Crystal dimensions 0.40x0.25x0.25 mm. Data were measured at 193 K on a Philips-PW1100 diffractometer with graphite monochromated Cu-Kα radiation. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give *R* = 0.044, *R*w = 0.069 for 2687 independent observed reflections $[|F_o| > 3\sigma(|F_o|]$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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