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DODECASUBSTITUTED PORPHYRINS – AN EASILY ACCESSIBLE TYPE OF DENDRITIC PORPHYRINS WITH TUNABLE PROPERTIES

Claudia Ryppa and Mathias O. Senge*

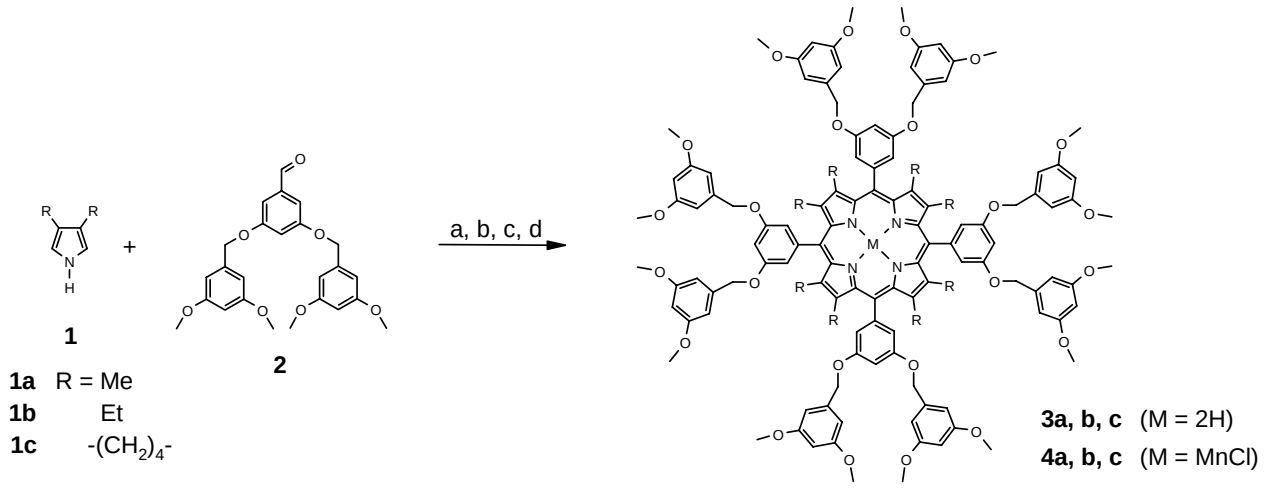
Institut für Chemie, Universität Potsdam, Karl-Liebknecht-Strasse 24-25, D-14476 Golm, Germany, mosenge@chem.uni-potsdam.de

Abstract – Dodecasubstituted dendritic porphyrins with nonplanar macrocycles were synthesized by a convergent approach *via* Lindsey condensation reactions in good yields.

Porphyrins with dendritic branches have a broad range of applications as oxidation catalysts,[1] models for electron transfer,[2] or mimics for biological functions (heme, Cyt c).[3,4] They have served as excellent examples for studying important physical properties such as redox potentials or adsorption characteristics. Further developments and optimisation of existing applications require the synthesis of new types of dendritic porphyrins with tailor-made physicochemical properties. One of the most fundamental approaches to vary the properties of chromophores is the fine-tuning of (photo)physical properties *via* conformational distortion of the macrocycles. The best examples, e.g. for variation of the redox potentials for applications in catalysis, are the so-called highly substituted porphyrins.[5] So far, no attempt has been made to develop a simple route for highly substituted, dendritic porphyrins that offers the potential to later combine the principles of shape-selective catalysis with the optimization of catalytic propereties, e.g. via stabilization of high-valent oxidation states. Although numerous dendritic porphyrins[6,7] with up to four susbtituents (either aryl or ester groups) in the meso position are known, only a few systems with more substituents have been reported in the literature.[7,8]

We wish to report a straightforward synthesis of dodecasubstituted dendritic porphyrins with a graded degree of conformational distortion. These porphyrins contain a β-alkylated porphyrin core with 3,5-bis(3,5-dimethoxybenzyloxy)phenyl branches in the meso position. First we tried to approach the target systems using a divergent approach. However, this turned out to be impractical for subsequent reactions due to incomplete etherification and purification problems that occur as a result of the steric hindrance present in β-substituted porphyrins.[9,10] The alternative convergent route includes first the synthesis of the

dendritic aldehyde (**2**)[10,11] and of the pyrrole derivatives (**1**),[12–14] followed by Lindsey condensation[15] (Scheme 1) to the favored porphyrin as the sole product similar to Fréchet *et al.*[10]



Scheme 1

Reagents and conditions: a) TFA, CH_2Cl_2, rt, Argon, 24 h in the dark. b) DDQ, rt, 1 h. c) NEt_3, rt, 10 min. d) $MnCl_2*4H_2O$, DMF, Δ

The yields are excellent, especially compared to the moderate yields typically obtained for other sterically hindered porphyrins[5] (yields: 29 % for **3a**, 34 % for **3b**, 41 % for **3c**).[16] Additionally, this approach is much shorter and more practical than syntheses utilizing subsequent modifications of pre-made porphyrins.[8] We surmise that the convergent synthesis for highly substituted porphyrins is a versatile approach for dendritic porphyrins which can be applied to later generations and other branches.

Table 1. UV/VIS absorption bands for selected compounds in CH_2Cl_2 with 1 % NEt_3. (Soret bands were underlined).

#	β R	Generation	λ_{max}					
3c	–$(CH_2)_4$–	1	277	<u>439</u>	531	573	611	675
3a	Me	1	277	<u>448</u>	544	588	628sh	690
3b	Et	1	277	<u>456</u>	553	598	637sh	695
–	Et	0	276	<u>455</u>	552	597	631	698
4c	–$(CH_2)_4$–	1	278	379	<u>491</u>	585	625	
4a	Me	1	278	383	<u>493</u>	591	630	
4b	Et	1	277	381	<u>496</u>	593	628	
–	Et	0	274	380	<u>495</u>	594	631	

A comparison of the absorption spectra (Table 1) of the first generation porphyrins (**3a-c**) shows a bathochromic shift of the absorption bands in line with the steric demand of the β-substituents (Et>Me>–$(CH_2)_4$–).[17] As bathochromic shifts are simple but reliable indicators for the macrocycle distortion and associated changes in redox potential and photophysics[5,18] this implies that the physicochemical properties can be fine-tuned in highly substituted dendritic free-base porphyrins in a

similar manner as in other more classical porphyrins with crowded substituents. A comparison with related structures of the 0. generation (i.e. with meso 3,5-dimethoxyphenyl residues) synthesized *via* a similar condensation (not shown) indicates that subsequent generations with longer branches might result in some "reflattening" of the macrocycles which is the focus of current investigations.

The spectroscopic differences between individual substituent types are much less pronounced in the corresponding Mn^{III} derivatives, which were prepared by standard metal insertion in good yields (~80 %). Evidently the manganese complexes are less conformationally flexible than the free base porphyrins and this has to be taken into account when designing potentially catalytically active dendrimer porphyrins.

In summary, Lindsey-type condensation reactions currently offer the best potential for preparing various highly substituted dendrimer porphyrins with targeted design of structure, macrocycle conformation, branch type and length, and fine-tuned physicochemical properties. Thus, the design principles developed for nonplanar porphyrins can easily be transferred to dendritic systems and used for applications in shape-selective catalysis and as superstructured materials.

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16. Selected analytical data: **3a** – mp 216 °C; ^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.62 (8H, *m*, $Ar_{o\text{-}\underline{H}}$), 7.15 (4H, *m*, $Ar_{p\text{-}\underline{H}}$), 6.81 (16H, *m*, $Bn_{o\text{-}\underline{H}}$), 6.54 (8H, *m*, $Bn_{p\text{-}\underline{H}}$), 5.36 (16H, br *s*, $OC\underline{H}_2$), 3.88 (48H, *s*, $OC\underline{H}_3$), 2.05 (24H, br *s*, $C\underline{H}_3$), -2.24 ppm (2H, br *s*, N<u>H</u>); ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 161.02 ($Bn_{m\text{-}\underline{C}}$), 159.01 ($Ar_{m\text{-}\underline{C}}$), 143.47 ($Ar_{i\text{-}\underline{C}}$), 139.25 ($Bn_{i\text{-}\underline{C}}$), 117.35 (*meso*-<u>C</u>), 115.28 ($Ar_{o\text{-}\underline{C}}$), 105.22 ($Bn_{o\text{-}\underline{C}}$), 102.55 ($Ar_{p\text{-}\underline{C}}$), 99.87 ($Bn_{p\text{-}\underline{C}}$), 70.17 ($O\underline{C}H_2$), 55.21 ppm ($O\underline{C}H_3$); UV/VIS ($CH_2Cl_2$, 1 % NEt_3, v/v): λ_{max} (log ε) = 277 (4.58), 448 (5.23), 544 (4.10), 588 (3.93), 628 (sh), 690 nm (3.57). **3b** – mp 233 °C; ^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.62 (8H, *m*, $Ar_{o\text{-}\underline{H}}$), 7.07 (4H, *m*, $Ar_{p\text{-}\underline{H}}$), 6.71 (16H, *m*, $Bn_{o\text{-}\underline{H}}$), 6.46 (8H, *m*, $Bn_{p\text{-}\underline{H}}$), 5.32, 5.20 (16H, *AB*, ^{2}J = 11.8 Hz, $OC\underline{H}_2$), 3.82 (48H, *s*, $OC\underline{H}_3$), 2.62, 2.20 (16H, *m*, $C\underline{H}_2CH_3$), 0.57 (24H, br *s*, $CH_2C\underline{H}_3$), -2.14 ppm (2H, br *s*, N<u>H</u>); ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 160.96 ($Bn_{m\text{-}\underline{C}}$), 158.15 ($Ar_{m\text{-}\underline{C}}$), 142.48 ($Ar_{i\text{-}\underline{C}}$), 139.26 ($Bn_{i\text{-}\underline{C}}$), 117.33 (*meso*-<u>C</u>), 115.64 ($Ar_{o\text{-}\underline{C}}$), 105.10 ($Bn_{o\text{-}\underline{C}}$), 102.72 ($Ar_{p\text{-}\underline{C}}$), 99.79 ($Bn_{p\text{-}\underline{C}}$), 70.21 ($O\underline{C}H_2$), 55.19 ($O\underline{C}H_3$), 17.03 ppm ($CH_2\underline{C}H_3$); UV/VIS ($CH_2Cl_2$, 1 % NEt_3, v/v): λ_{max} (log ε) = 277 (4.59), 456 (5.14), 553 (4.06), 598 (3.87), 637 (sh), 695 nm (3.60); MS (pos. FAB): m/z = 2167 (100 %, $[M - H]^+$), 2138 (8 %, $[M - OCH_2]^+$), 2017 (28 %, $[M - C_9H_{11}O_2]^+$), 2002 (8 %, $[M - C_9H_{11}O_2 - CH_3]^{\bullet+}$), 1864 (3 %, $[M - 2\ C_9H_{11}O_2]^{\bullet+}$), 1084 (7 %, $[M]^{2+}$). **3c** – mp 224 °C; ^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.48 (8H, *m*, $Ar_{o\text{-}\underline{H}}$), 7.07 (4H, *m*, $Ar_{p\text{-}\underline{H}}$), 6.73 (16H, *m*, $Bn_{o\text{-}\underline{H}}$), 6.46 (8H, *m*, $Bn_{p\text{-}\underline{H}}$), 5.29 (16H, br *s*, $OC\underline{H}_2$), 3.82 (48H, *s*, $OC\underline{H}_3$), 2.48 (16H, br *s*, $C\underline{C}H_2CH_2$), 1.53 (16H, br *s*, $CCH_2C\underline{H}_2$), -2.49 ppm (2H, br *s*, N<u>H</u>); ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 160.99 ($Bn_{m\text{-}\underline{C}}$), 159.67 ($Ar_{m\text{-}\underline{C}}$), 143.46 ($Ar_{i\text{-}\underline{C}}$), 139.35 ($Bn_{i\text{-}\underline{C}}$), 116.58 (*meso*-<u>C</u>), 114.80 ($Ar_{o\text{-}\underline{C}}$), 105.15 ($Bn_{o\text{-}\underline{C}}$), 102.67 ($Ar_{p\text{-}\underline{C}}$), 99.83 ($Bn_{p\text{-}\underline{C}}$), 70.07 ($O\underline{C}H_2$), 55.24 ($O\underline{C}H_3$), 25.48 ($C\underline{C}H_2CH_2$), 23.50 ppm ($CCH_2\underline{C}H_2$); UV/VIS ($CH_2Cl_2$, 1 % NEt_3, v/v): λ_{max} (log ε) = 277 (4.55), 439 (5.25), 531 (4.23), 573 (3.75), 611 (3.70), 675 nm (3.30); MS (ESI): m/z = 1085 (100 %, $[M]^{2+}$), 150 (33 %, $[C_9H_{11}O_2]^{\bullet+}$.
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