

## Octopus Manganese Porphyrin with Polyglycol Chains as a Catalyst for the $\alpha$ -Selective Epoxidation of Cholesterol Derivatives

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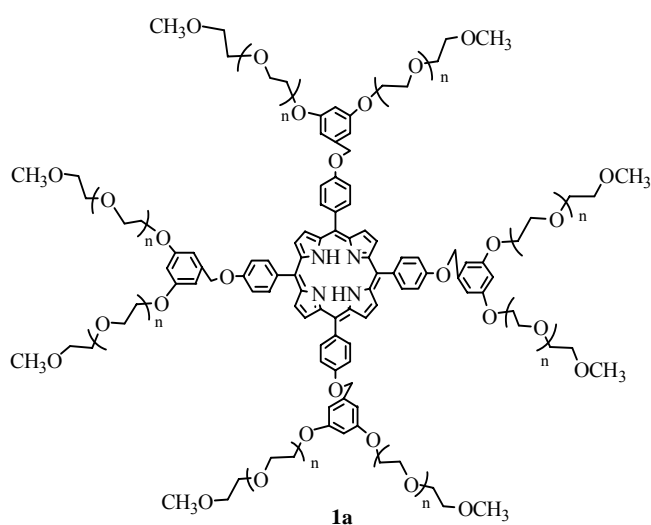
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**Abstract:** Synthesis of a novel octopus porphyrin with polyglycol chains **1a** was achieved. The catalytic activity of **1a**'s manganese complex for the epoxidation of cholesterol derivatives with PhIO give a satisfactory conversion and regioselectivity.

**Keywords:** Octopus porphyrin, synthesis, epoxidation, cholesterol derivatives.

Recently the biologic and catalytic activity of dendritic macromolecule metal complexes have been paid more and more attention<sup>1,2</sup>. It inspired us to design the novel octopus porphyrin **1a** as shown in **Scheme 1**. **1a** reacts with  $Mn(OAc)_2$  to form the complex of manganese porphyrin **1b**, which can catalyze the epoxidation of cholesterol derivatives using PhIO as oxidant. The reaction was highly  $\alpha$ -selective.

**Scheme 1**

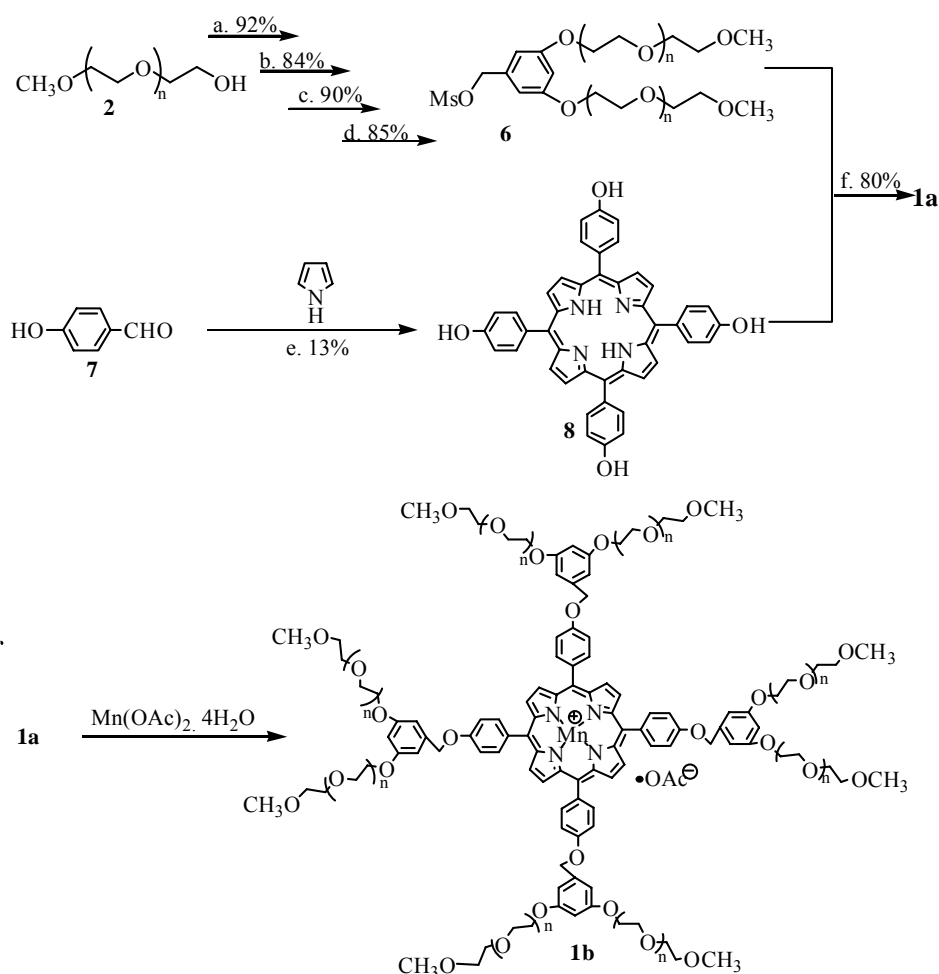


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## Results and Discussion

From the convergent approach method for general dendrimer synthesis<sup>3</sup>, we synthesized the octopus porphyrin **1a**. The synthetic route of **1a**<sup>4</sup> and its manganese complex **1b**<sup>5</sup> is described as follows.

Scheme 2



Reagents and conditions: a.  $\text{CH}_3\text{SO}_2\text{Cl}$ ,  $\text{NEt}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $-10^\circ\text{C}$ ; b. methyl 3,5-dihydroxy benzoate,  $\text{K}_2\text{CO}_3$ , acetone, overnight reflux; c.  $\text{LiAlH}_4$ , THF, reflux 2 h; d.  $\text{CH}_3\text{SO}_2\text{Cl}$ ,  $\text{NEt}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $-10^\circ\text{C}$ ; e. propanic acid,  $136^\circ\text{C}$ , 20 min; f.  $\text{K}_2\text{CO}_3$ , DMF,  $80^\circ\text{C}$ , 6 h.

Dendrimer **6** can be easily produced from polyethylene glycol monomethyl ether (PEG400, MW 428) **2** by four steps in turn<sup>6</sup>. Octopus porphyrin **1a** was obtained by a coupling reaction of four equivalents of dendrimer **6** to one equivalent of 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin **8**<sup>7</sup>. **1a** was reacted with manganese(II) acetate in *N,N*-dimethylformamide to produce octopus manganese porphyrin complex **1b**.



**References and Notes**

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4. Compound **1a**:  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$ (ppm): 7.74 (d, 8H,  $J=8\text{Hz}$ , Ph-H), 7.33 (d, 8H,  $J=8\text{Hz}$ , Ph-H), 6.86 (s, 8H, Ph-H), 6.78 (s, 4H, Ph-H), 6.59-6.40 (m, 8H, Pyrrol-H), 5.28 (s, 8H,  $\text{OCH}_2\text{Ph}$ ), 3.67-3.50 (m,  $\text{OCH}_2$ -, N-H), 3.37 (s, 24H,  $\text{CH}_3\text{O}$ -); IR (KBr,  $\text{cm}^{-1}$ ): 3484 (NH), 2872 ( $\text{CH}_2$ ), 1596 (Ar-H), 1108 (C-O-C); UV/Vis ( $\lambda_{\text{max}}$ ,  $\text{CHCl}_3$ , nm): 421(soret), 518, 555, 650.
5. Synthesis of **1b**: A mixture of **1a** (668 mg, 0.15 mmol),  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (98 mg, 0.4 mmol) and DMF (40 mL) was refluxed for 24 h, then distilled to dryness under reduced pressure. To the residue was added dichloromethane (30 mL). The solid was filtrated off. The filtrate was washed with water ( $3 \times 10$  mL), dried over  $\text{Na}_2\text{SO}_4$  and evaporated to dryness. The residue was chromatographed on silica gel with methanol/dichloromethane (1:10) as the eluent to get green product (466 mg), yield 69%. The content of manganese 0.18 mmol/ 1 g **1b**. UV/Vis ( $\lambda_{\text{max}}$ ,  $\text{CHCl}_3$ , nm): 481 (soret), 587, 624.
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9. Procedure for epoxidation of alkenes catalyzed by octopus manganese porphyrin **1b** using PhIO as oxidant. A mixture of alkene (20 mg, 0.046 mmol), PhIO (12.3 mg, 0.056 mmol), and **1b** (0.17 mg,  $3.7 \times 10^{-5}$  mmol) in  $\text{CH}_2\text{Cl}_2$  (4 mL) were stirred at room temperature. When the reaction was completed (detected by TLC). The solid was filtrated off. The filtrate was evaporated *in vacuo* to remove the solvent and the residue was analyzed by  $^1\text{H-NMR}$ (400 MHz) to determine the conversion, yield and selectivity.
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