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Synthesis of PAMAM Dendrimers Bearing BINOL Derivative

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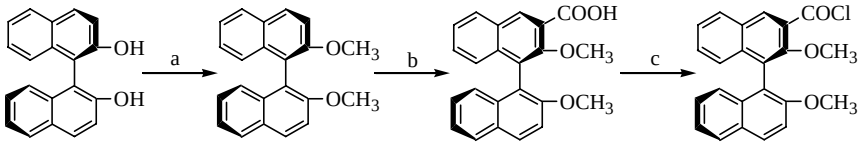
Abstract: New functional dendrimers bearing 4, 8 and 16 axial chiral units on their surface were synthesized from achiral PAMAM dendrimers and axial chiral (R)-BINOL derivative.

Keywords: Chiral dendrimers, synthesis, BINOL.

The chemistry of dendrimers is blossoming into an exciting field of research. A wide varity of dendrimers with different cores, branches, and end groups have been synthesized and applied to different areas, such as in drug delivery, catalysis, molecular recognition, light harvesting, sensors and environmental studies, during the past decade[1]. Now, application of functionalized dendrimers has attracted the attention of a number of researchers[2]. Chiral functionalities can be tethered to the dendritic branches and the resulting chiral dendrimers that work as dendritic chiral ligands in chiral recognition[3]. Every chiral site at the periphery would work effectively with approximately the same effect and efficiency. It would be expected that the chiral dendrimers have more excellent characteristics than other polymer-supported chiral ligands[4].

Scheme 1



1 **2** **3** **4**

(a) CH_3I, K_2CO_3, CH_3COCH_3, 97%; (b) *n*-BuLi, -78 ℃; then dry CO_2, 0℃, 34%; (c) $SOCl_2$, reflux.

It is well known that axially dissymmetric 1, 1′-binaphthalene derivatives serve as highly efficiency chiral inducers for a wide range of asymmetric reactions and have excellent chiral recognition property[5]. Diphenyl-substitued 1,1′-binaphthyl crown ether and polymer-supported BINOL have been widely used to chiral stationary phases (CSPs)

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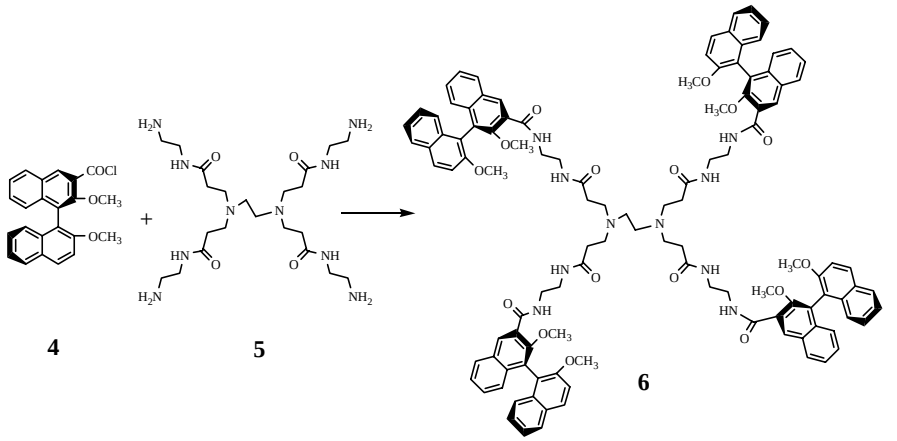
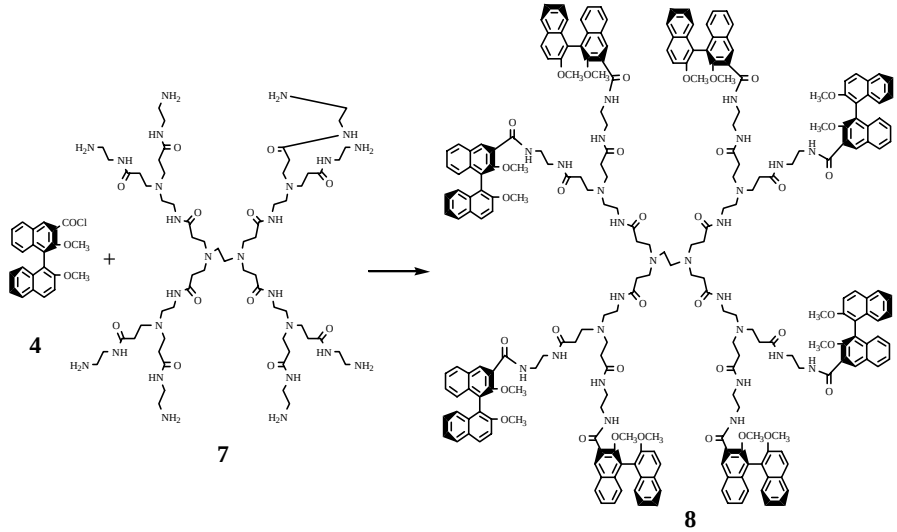
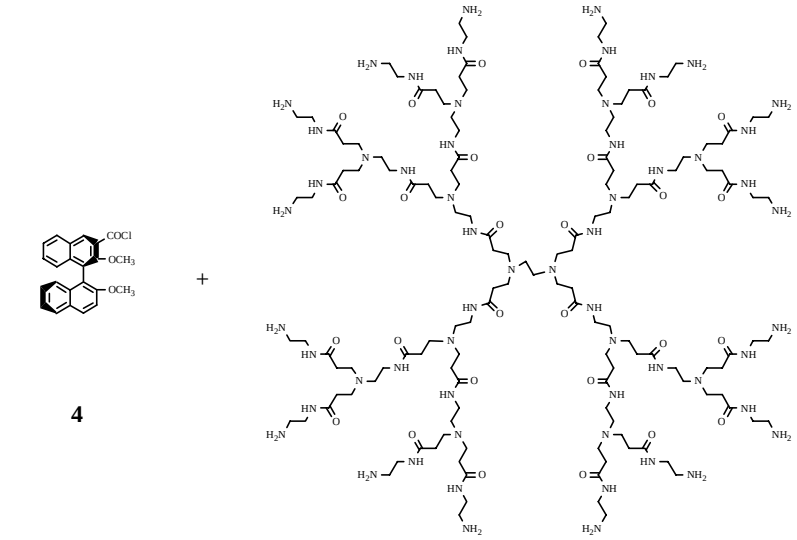
for high-performance liquid chromatography (HPLC)[6].

Here, we reported the synthesis of chiral dendrimers **6**, **8** and **10**, bearing four, eight and sixteen chiral derivative of 2,2′-dihydroxy-1,1′-binaphthalene (BINOL)[7], respectively. The coupled derivative of (R)-BINOL **4** was synthesized as shown in **Scheme 1**. The hydroxyl group of (R)-BINOL **1** was protected by methyl ether to give **2**. **2** was lithiated in THF at –78 °C using 1.2 e.q. *n*-BuLi, after 3 hr dry CO_2 was added to afford **3**. **3** was refluxed with $SOCl_2$ for 4 hr to give **4**. The synthetic route of chiral dendrimers is outlined in **Scheme 2**. The synthetic procedure for **8** is representative. To a stirred solution of PAMAM G1.0 **7** (0.29 g, 0.2 mmol) and triethylamine (0.32 g, 3.2 mmol) in DMAc (10 mL) was added **4** (1.21 g, 1.6 mmol) in portions at room tem-

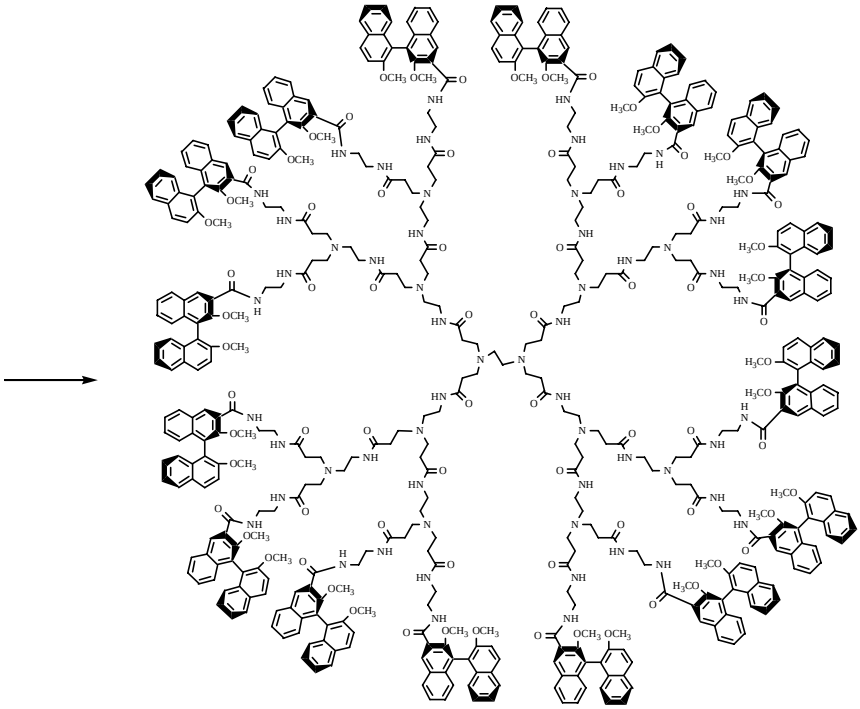
Scheme 2







4 **9**



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perature under nitrogen atmosphere. After stirring at 40°C for 36 hr, the reaction mixture was filtrated. The filtrate was dropped into 200 mL of diethyl ether with stirring. The resultant precipitate was collected by filtration and washed with diethyl

ether. The precipitation procedure was repeated twice and afforded dendrimer **8** as gray solid**.** The structures of **2**~**10** were confirmed by IR, ^{1}H NMR and MS spectra. The representative dendrimer **8** gave the data as follows: yield 75% based on PAMAM G1.0 **7**; $[\alpha]_{25}^{D}$ +78.9 (c 0.1, DMF); IR (KBr) 3289, 2939, 1651, 1267, 1249, 1019, 811, and 753 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$) δ 2.3-3.8 (m, 148H), 7.0-8.7 (m, 108H); MS found *m/z* 4152.8, calcd. for $C_{246}H_{256}N_{36}O_{26}$ (M+1): 4153.9.

In summary, a new type of chiral dendrimers was synthesized. Their application to chiral stationary phases (CSPs) for high-performance liquid chromatography (HPLC) is in progress.

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