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Efficient Synthesis of Dendritic Architectures by One-Pot Double Click Reactions

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Dendritic macromolecules with 8 and 16 hydroxy end-groups on the periphery have been synthesized using double click reactions (Cu-catalyzed azide/alkyne click chemistry, i.e., CuAAC and Diels–Alder [4 + 2] cycloaddition reactions) with a one-pot technique. The structure of the dendrimers was characterized by ¹H and ¹³C NMR spectroscopy, and matrix-assisted laser desorpton–ionization time-of-flight mass spectrometry. The purity was determined by size exclusion chromatography.

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Introduction

Dendrimers^[1–3] are a class of monodispersed macromolecules with a regular and highly branched three-dimensional architecture. The size, the number of end groups, and the functionality are tailored, which enables their properties to be tuned precisely. Therefore, dendrimers have emerged as attractive nanometer-scale subjects for various applications such as molecular light harvesting,^[4,5] drug delivery,^[6–10] homogeneous catalysis,^[11–15] etc. In recent years, another important application of dendrimers is to use well-defined dendrons as the building blocks to construct dendronized polymers with a one-dimensional structure in macromolecular chemistry.^[16–20]

In general, there are two synthetic strategies to synthesize dendrimers. The first route is known as the divergent growth approach,^[21,22] i.e., the divergent generation of dendrons through repetitive growth and activation steps from a central core. The second route is a convergent approach.^[23] By this strategy, perfect dendrons are coupled onto a preformed functional centre. However, with the generation increase, these two synthetic strategies face the shortcomings of incomplete grafting and low yields, respectively. Fortunately, by the combination of divergent and convergent approaches, namely using an orthogonal procedure, one can produce dendrimers with defectfree structures in good yields. Chemical reactions with highly efficient selection, strong tolerance of functional groups, and quantitative yield are usually employed in this strategy.

Recently, the 'click' reaction concept, mainly exemplified by Cu-catalyzed azide/alkyne click chemistry, i.e., CuAAC,^[24,25] has attracted considerable attention in polymer chemistry because it meets the requirement for the orthogonal synthesis of polymeric materials through accelerated synthetic strategies.^[26,27] For example, linear and mikto-arm star polymers have been synthesized by combining CuAAC and controlled radical polymerization (CRP), such as atom transfer radical polymerization (ATRP),^[28,29] and nitroxide-meditated polymerization (NMP).^[30]

More importantly, the orthogonality of CuAAC has also allowed the reaction to be combined with Diels-Alder [4+2]

cycloaddition reactions. These two different kinds of reactions, in which orthogonal reactive groups are 'clicked' together with high efficiency, have been extensively applied to polymer chemistry, to produce a range of polymeric materials varying from dendrimers, $[^{31-35}]$ to block polymers, $[^{36-39}]$ star polymers, $[^{40-45}]$ and other complex polymers. $[^{46-51}]$

The orthogonal combination of CuAAC and Diels-Alder [4+2] cycloaddition reactions (namely double click reactions) has received great attention from academia.[52-54] Herein, we report an orthogonal approach to defect-free dendrimer derivatives of the classical Fréchet-type and 2,2-bis(methylol)propionic acid (bis-MPA) dendritic macromolecules using double click reactions with a one-pot technique. As shown in Scheme 1, the whole synthetic process of this work is carried out through the following steps: (i) preparation of an alkyne-modified central core by Williamson etherification; (ii) attachment of anthracene groups onto the central core by CuAAC and then postmodification of the anthracene functional core through a Diels-Alder [4 + 2] cycloaddition with a one-pot technique; and (iii) mild and efficient cleavage of the isopropylidene protecting groups on the periphery of the intermediates 6a and 6b. By this strategy, bis-MPA dendrons may be grafted onto the functional dendrimers through an accelerated method and this process can also be monitored easily using UV and fluorescence measurements. The details of the above procedures and the results obtained will be discussed in the next section.

Results and Discussion

Synthesis of Alkyne-Modified Fréchet-Type Dendron 3

Compound **3** was synthesized by the Williamson etherification of bisphenol-A with an excess of Fréchet-type **[G1]-Br** in the presence of K₂CO₃ in acetone (see Scheme S1 in the Accessory Publication for the synthesis of **3**). The structure of **3** was confirmed by ¹H and ¹³C NMR spectroscopy and matrix-assisted laser desorption–ionization time-of-flight (MALDI-TOF) mass spectrometry. In the ¹H NMR spectrum of **3**, the single peak at 2.50 ppm corresponded to the proton of $-C\equiv$ CH. The single peaks at 1.63, 4.65, and 4.97 ppm, respectively, were assigned



Scheme 1. Structure of building blocks and strategy to prepare hydroxy-group modified dendrimers 7a and 7b by one-pot double click reactions.



Fig. 1. ¹H NMR spectrum of dendrimer **6a** in CDCl₃ with assignment.

to the protons of $-CH_3$, $-OCH_2C\equiv CH$, and $-CH_2O$. The carbon signals of the $-C\equiv C$ group were observed at 76.68 and 79.21 ppm in the ¹³C NMR spectrum. The signal at 56.83 ppm was assigned to the carbon of C-4 of $-OCH_2C\equiv CH$. The carbon signal of C-1 of the methyl appeared in the ¹³C NMR spectrum at 31.93 ppm. The carbon signal at 70.57 ppm corresponded to C-3 of $-OCH_2Ar$. The other correlative signals could be assigned to the corresponding protons and carbons of **3** as shown in Figs S1 and S2 of the Accessory Publication.

One-Pot Synthesis of Dendrimers **6a** and **6b** by a Double Click Reaction

In this step, compound **3**, azide-functionalized anthracene **4**, and bis-MPA dendrons **5a** or **5b** were reacted in one pot in order to produce the corresponding dendrimer **6a** or **6b** by double click reactions (Scheme 1). During the process, excess amounts of **4** (3.5 mmol, 1.1 equiv.) and **5a** or **5b** (6.4 mmol, 2.0 equiv.) are used compared with that of **3** (0.8 mmol). A click reaction was accomplished between the azide of **4** and the alkyne group of dendron **3** catalyzed by CuBr/pentamethyldiethylenetriamine (PMDETA) in *N*,*N*-dimethylformamide (DMF) at room temperature. When the reaction was completed, the reaction mixture was heated to 110°C and continued to stir for 3 h. During this process, a Diels–Alder [4+2] reaction was accomplished between the anthracene group of the intermediate and the bis-MPA dendrons **5a** or **5b**.

Evidence for the occurrence of the double click reactions was obtained from ¹H NMR, ¹³C NMR, UV, and fluorescence spectroscopy. The ¹H NMR spectrum of dendrimer **6a** is shown in Fig. 1 (see Fig. S3 in the Accessory Publication for the ¹H NMR spectrum of **6b**, and see Figs S4–S5 for the ¹³C NMR spectra of

6a and **6b**, respectively). As can be seen from Fig. 1, the peaks between 7.60 and 8.40 ppm, characteristic for aromatic protons of anthracene, completely disappear, which clearly indicates the quantitative efficiency of the process. It reveals the loss of the aromaticity of the central phenyl units of anthracene as a result of the Diels–Alder cycloaddition. At the same time, the single peak at 2.50 ppm also completely disappears, which represented the $-C \equiv CH$ proton. Furthermore, a double peak appeared at approximately 4.74 ppm, which is attributable to the bridgehead proton of the cycloadduct H-14. The peaks at 3.56 and 4.10 ppm were assigned to H-8 and H-11 of the bis-MPA dendron, respectively. The distinct signals at 1.13, 1.33, and 1.37 ppm correspond to H-9 and H-13 of the methyl groups in the bis-MPA dendron. These results reveal that the synthesis of dendrimer **6a** by a one-pot double click reaction was achieved efficiently.

The Diels–Alder [4 + 2] cycloaddition was monitored by UV spectroscopy. In order to obtain a direct comparison easily, the intermediate anthracene derivative 4' of the CuAAC reaction was isolated, whose detailed structural analysis is shown in Figs S6–S7. In the UV spectra (Fig. 2 for 4' and 6a, and Fig. S8 for 4' and 6b), although compound 4' displayed a characteristic five-finger absorbance in the range of 300–400 nm, the dendrimer 6a showed no absorbance in the same region (Fig. 2b), which was caused by the loss of the aromaticity of the central phenyl unit of anthracene.

Fluorescence spectra might also provide further evidence for the efficiency of the Diels–Alder reaction (Fig. 2 for 4' and 6a, and Fig. S9 for 4' and 6b). Fig. 2 (right) shows the fluorescence spectra of the intermediate 4' before and after reaction with the bis-MPA dendron. The characteristic fluorescent band of the anthracene group between 350 and 500 nm disappears

completely after the Diels-Alder reaction. Based on the above results of ¹H NMR, UV, and fluorescence measurements, it is clear that a quantitative Diels-Alder reaction has occurred between the anthracene and bis-MPA dendron. That is to say, the bis-MPA dendrons have been attached to the central core successfully by a Diels-Alder reaction between anthracene and maleimide derivatives.

Deprotection of Dendrimers 6a and 6b

0.9

0.6

0.3

0.0

Absorbance

The isopropylidene groups of -OH groups in two dendrimers could be removed using Dowex H⁺ resin in a mixture of tetrahydrofuran (THF) and MeOH. The hydrolyzed products were confirmed by ¹H and ¹³C NMR spectroscopy.

The partial ¹H NMR spectra (Fig. 3b) confirmed that the isopropylidene groups have been completely removed based on the disappearance of the resonance of signals at 1.33 and 1.37 ppm,

(b)

which were assigned to H-1 and H-2 of the methyl group (see Fig. S10 for the ¹H NMR spectrum of **7b**). Furthermore, no signals for C-1, 2, and 3 of the protective groups at 23.03, 25.11, and 98.94 ppm in the ¹³C NMR spectrum were found (Fig. S11b), which indicates that the protective groups were removed completely from the dendrimer 6a (see Fig. S12 for the ¹³C NMR spectrum of 7b).

Size exclusion chromatography (SEC) was applied to characterize the purity of the building blocks (3, 5b) and the dendrimers (6b, 7b). As demonstrated in Fig. 4, monodisperse peaks were obtained $(1.01 \le M_w/M_n \le 1.08)$, which indicates that the click reaction and separation were efficient (see Fig. S13 for the SEC traces of 3, 5a, 6a, and 7a). The actual molar masses were determined by MALDI-TOF mass spectrometry, and the observed molecular weight agreed with the theoretical values. For example, the MALDI-TOF mass spectrum of 7b (Fig. 5) showed a single peak at m/z 3538, which is the molecular ion peak with

(b)

320 360 400 440 400 450 500 550 600 Wavelength [nm] Wavelength [nm]

750

600

300

150

0

ntensity [a.u.] 450

Fig. 2. Comparison of UV/Vis (left) and fluorescence spectra (right, λ_{exc} 350 nm) of 4' (a) and 6a (b) in THF (5.0 × 10⁻⁵ M for UV/Vis and 2.0 × 10⁻⁵ M for fluorescence spectra, 25°C).



Fig. 3. The partial ¹H NMR spectra of **6a** (a) and **7a** (b) in CDCl₃.

sodium $[M + Na]^+$ (see Fig. S14 for the MALDI-TOF mass spectrum of **7a**). Detailed characterization information of **6a**, **6b**, **7a**, and **7b** is collected in Table 1.

Conclusions

In this work, we have demonstrated a versatile synthesis of dendrimers that contain functional groups, such as hydroxy groups, on the dendritic periphery, by efficiently combining CuAAC and Diels–Alder [4+2] cycloaddition strategies with a onepot technique. Based on NMR, mass spectrometry, SEC, and fluorescence analysis, we confirm the formation of a class of defect-free dendrimers. This facile modular synthetic method can, furthermore, afford the production of dendrimers with different compositions and functions.

Experimental

Materials

Bisphenol-A (tech 97%, Alfa), 9-anthracenemethanol (tech 98%, Alfa), propargyl bromide (80% in toluene, Alfa), sodium azide (AR, Beijing Chemicals Co.), lithium tetrahydroaluminate (typically 97%, Alfa), and sodium hydride (60% dispersed in mineral oil, Aldrich) were used as received. Maleic anhydride (MAn) was recrystallized from benzene. Other reagents



Fig. 4. Size exclusion chromatography traces of building blocks 3 (trace b), 5b (trace a), and the dendrimers 6b (trace c), and 7b (trace d).

were used without further purification. Compounds **5a** and **5b** were prepared (all of purity \geq 98%) according to literature procedures.^[20]

Instruments

NMR spectra were acquired in CDCl₃ on a Bruker DMX-400 spectrometer at 400 MHz for ¹H NMR and 100 MHz for ¹³C NMR, the chemical shifts are given in δ values from tetramethyl-silane (TMS) as an internal standard. SEC using polystyrene as a standard was performed on a Waters 2414 instrument with THF as an eluent at a flow rate of 1.0 mL min⁻¹. Fluorescence spectra were recorded on a Varian Cary-Eclipse spectrophotometer. MALDI-TOF mass spectrometry was performed on a Bruker Biflex III spectrometer equipped with a 337 nm nitrogen laser. Mass spectra were acquired in positive reflector mode using an acceleration voltage of 19 kV.

Synthesis of Alkyne-Modified Fréchet-Type Dendron 3

Bisphenol-A (0.71 g, 3.01 mmol), anhydrous potassium carbonate (2.0 g, 14.5 mmol), **[G1]-Br** (1) (2.0 g, 7.16 mmol), and potassium iodide (120 mg, 0.72 mmol) were refluxed in dry acetone (20 mL) under N₂ for 48 h. The solution was evaporated to dryness, and the residue partitioned between dichloromethane (DCM, 100 mL) and water (100 mL). The organic layer was separated, and the aqueous phase extracted with DCM (3 × 20 mL). The combined organic phase was dried (Na₂SO₄), filtered, and evaporated to give a fawn product. The crude product was purified by column chromatography (SiO₂, DCM/petroleum ether (PE), 1/4, v/v). The alkyne-modified compound **3** was isolated as a white solid (1.34 g, 70%). $\delta_{\rm H}$ 1.63 (s, 6H, 2 × CH₃), 2.50

 Table 1. Characterization data of molar masses and polydispersities from mass spectra (MALDI-TOF) and SEC of 6a, 6b, 7a, and 7b

ersity index
.05
.05
.05
.08

^ACalculated according to the atom weight. ^B $[M]^+$.

 ${}^{C}[M+K]^{+}.$



Fig. 5. Matrix-assisted laser desorpton-ionization time-of-flight mass spectrometry spectrum of 7b.

(s, 4H, 4 × C≡CH), 4.65 (s, 8H, 4 × OCH₂C≡CH), 4.97 (s, 4H, 2 × CH₂O), 6.55–7.14 (m, 14H, H-Ar). $\delta_{\rm C}$ 31.93 (2C, CH₃), 42.60 (1C, *C*(CH₃)₂), 56.83 (4C, OCH₂C≡CH), 70.57 (2C, OCH₂Ar), 76.68 (4C, C≡CH), 79.21 (4C, *C*≡CH), 102.54, 107.70, 115.10, 128.66, 140.76, 144.37, 157.36, 159.72 (C-Ar). *m/z* (MALDI-TOF) 647.0 [M + Na]⁺, 663.0 [M + K]⁺.

One-Pot Synthesis of Dendritic Architectures

Compound 3 (0.50 g, 0.80 mmol), azide-functionalized anthracene 4 (0.82 g, 3.50 mmol), and bis-MPA dendron 5a or 5b (6.40 mmol, 2.0 equiv.) were dissolved in nitrogen-purged DMF (10 mL) in a Schlenk flask, CuBr (46.0 mg, 0.32 mmol, 0.1 equiv.) and PMDETA (55.4 mg, 0.32 mmol, 0.1 equiv.) were added, and the reaction mixture was degassed by three freezepump-thaw cycles and left under nitrogen and stirred at room temperature for 12 h. The reaction mixture was then stirred at 110°C for 3 h. When the reaction was completed, the mixture was evaporated under high vacuum. The crude product obtained was then dissolved in 5.0 mL of THF and passed through an alumina column to remove the copper salt. The solution was evaporated to give a crude product, which was purified by column chromatography (SiO₂, DCM/PE, 1/3, v/v). The dendrimer 6a or 6b was isolated as a white solid (the yields were 73 and 65%, respectively).

Compound **6a**: $\delta_{\rm H}$ 1.13 (s, 12H, 4 × CH₃), 1.33 (s, 12H, 4 × CH₃), 1.37 (s, 12H, 4 × CH₃), 1.62 (s, 6H, 2 × CH₃), 3.14– 3.28 (m, 8H, H-10, 12), 3.37 (t, J 5.50, 8H, 4 × NCH₂), 3.56 (d, J 11.80, 8H, H-8, 11), 3.61 (t, J 5.45, 8H, H-7), 4.10 (d, J 11.80, 8H, H-8, 11), 4.74 (d, J 2.90, 4H, H-14), 4.92 (s, 4H, H-2), 5.16 (s, 8H, H-3), 5.86 (dd, 8H, H-5), 6.67–7.35 (m, 42H, H-Ar), 8.25 (s, 4H, H-4), 8.35 (s, 4H, H-Ar). $\delta_{\rm C}$ 19.43, 23.53, 25.51, 26.50, 31.94, 38.09, 42.60, 46.66, 47.02, 48.40, 48.98, 49.93, 61.96, 62.88, 66.70, 66.75, 68.86, 70.59, 98.95, 107.55, 115.01, 122.20, 124.86, 125.65, 126.56, 127.08, 127.74, 127.96, 128.15, 128.36, 128.66, 139.71, 139.85, 140.85, 142.64, 144.33, 160.45, 174.72, 176.70, 177.04. *m/z* (MALDI-TOF) 2747.4 [M]^{+•}, 2768.4 [M + Na]⁺.

Compound **6b**: $\delta_{\rm H}$ 1.09 (s, 12H, 4 × CH₃), 1.10 (s, 12H, 4 × CH₃), 1.25 (s, 24H, 8 × CH₃), 1.27 (s, 12H, 4 × CH₃), 1.36 (s, 12H, 4 × CH₃), 1.37 (s, 12H, 4 × CH₃), 1.62 (s, 6H, 2 × CH₃), 3.23 (d, 4H, *J* 8.48, H-10), 3.31–3.36 (m, 12H, 4 × NCH₂, H-12), 3.56–3.60 (m, 24H, H-8, 11, 15, and 17), 4.08–4.27 (m, 32H, H-7, 8, 11, 15, and 17), 4.74 (d, *J* 2.68, 4H, H-14), 4.91 (s, 4H, H-2), 5.15 (s, 8H, H-3), 5.90 (dd, 8H, H-5), 6.67–7.35 (m, 42H, H-Ar), 8.18 (s, 4H, H-4), 8.34 (s, 4H, H-Ar). $\delta_{\rm C}$ 12.30, 14.99, 15.19, 18.38, 19.35, 19.40, 20.31, 21.30, 22.63, 22.69, 23.50, 23.51, 26.20, 29.92, 32.45, 42.21, 42.89, 42.92, 46.67, 47.59, 48.55, 49.02, 62.82, 62.84, 66.09, 66.81, 98.94, 115.00, 122.29, 124.83, 125.63, 126.50, 127.16, 127.66, 127.89, 128.07, 128.27, 128.64, 135.12, 139.86, 139.99, 140.97, 142.70, 144.22, 157.39, 160.51, 172.96, 174.45, 176.94, 177.20. *m/z* (MALDI-TOF) 3859.2 [M + Na]⁺, 3875.2 [M + K]⁺.

General Procedure for the Hydrolysis of 6a and 6b

The protected dendrimer **6a** or **6b** (0.18 mmol) was dissolved in a mixture of THF and MeOH (3/1, v/v, 10 mL) and three teaspoons of Dowex H⁺ resin were added, the reaction mixture was stirred for 3 h at room temperature. When the reaction was complete, the Dowex H⁺ resin was filtered off in a glass filter and carefully washed with THF. The solution was evaporated to give a pale solid **7a** or **7b** (the yields were 91 and 90%, respectively).

Compound **7a**: $\delta_{\rm H}$ 0.99 (s, 12H, 4 × CH₃), 1.60 (s, 6H, 2 × CH₃), 3.12–3.34 (m, 24H, H-6, 10, 12, and –OH), 3.63–3.71 (m, 24H, H-7, 8, and 11), 4.71 (s, 4H, H-14), 4.88 (s, 4H, H-2), 5.14 (s, 8H, H-3), 5.86 (dd, 8H, H-5), 6.57–7.31 (m, 42H, H-Ar), 8.19 (s, 4H, H-4), 8.37 (s, 4H, H-Ar). $\delta_{\rm C}$ 17.31, 31.10, 37.74, 45.82, 46.22, 47.62, 48.20, 49.16, 49.66, 61.74, 62.09, 67.29, 69.80, 106.90, 114.26, 121.38, 124.10, 124.83, 125.72, 126.55, 126.92, 127.18, 127.34, 127.52, 127.89, 128.90, 131.23, 138.93, 139.17, 140.05, 141.89, 143.49, 143.61, 156.51, 159.59, 175.32, 176.54. *m/z* (MALDI-TOF) 2609.1 [M + Na]⁺.

Accessory Publication

Scheme S1 of the synthesis of alkyne-modified compound **3**, Figs S1–S2 of the ¹H and ¹³C NMR spectra of compound **3**, Fig. S3 of the ¹H NMR spectrum of **6b**, Fig. S4 of the ¹³C NMR spectrum of **6a**, Fig. S5 of the ¹³C NMR spectrum of **6b**, Figs S6–S7 of the ¹H and ¹³C NMR spectra of compound **4'**, Figs S8–S9 of the UV/vis and fluorescence spectra of **4'** and **6b**, Fig. S10 of the ¹H NMR spectrum of **7b**, Fig. S11 of the partial ¹³C NMR spectra of **6a** and **7a**, Fig. S12 of the ¹³C NMR spectrum of **7b**, Fig. S13 of the SEC traces of **3**, **5a**, **6a**, and **7a**, and Fig. S14 of the MALDI-TOF MS spectrum of **7a** are available from the Journal's website.

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