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Dendrimers

High-Generation Second-Order Nonlinear Optical (NLO) Dendrimers: Convenient Synthesis by Click Chemistry and the Increasing Trend of NLO Effects**

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Dendrimers are defect-free and perfect monodisperse macromolecules with a regular and highly three-dimensional branched structure, which can bring out many special properties: nanometer size, globular shape, multivalent character, and modularity of the assembly. These characteristics make them competitive candidates for applications in a variety of fields including catalysis, biology, and materials science.[1–3] Generally, highly branched dendrimers could be constructed through a divergent (a growing pattern from a multivalent core) or convergent (a dendron is grafted on to the core) synthetic strategy.[1] However, the tedious multistep synthetic protocols often make the preparation of dendrimers relatively costly and involve some difficulties, such as the incomplete reaction of the end groups in the divergent approach (leading to the structural defects) and steric hindrance between the reactive segments and core molecule (hampering the formation of high generations) in the convergent strategy.[2b] Versatile methodologies to address these issues have now rendered the synthesis of dendrimers more precise and economical.[2c] As typical examples, through the combination of the divergent and convergent approaches (a "double-stage" method),[4] proposed by Fréchet and co-workers,[4a] the synthetic efficiency could be raised rapidly; also, by the utilization of the powerful Cu^{I}-catalyzed 1,3-dipolar cycloaddition reactions between azides and alkynes (the Sharpless "click" reaction),[5] many divergently built-up dendrimers were yielded after the pioneering work of Fréchet and co-workers.[6–8] However, there are currently very few reports of the use of "click chemistry" for both parts of a combined divergent and convergent approach.

The development of organic second-order nonlinear optical (NLO) materials is motivated by the promising of performance and cost improvements related to telecommunications, computing, embedded network sensing, terahertz wave generation and detection, and many other applications.[9,10] One major obstacle that hinders the rapid development of this field is efficient translation of the large β values of the organic chromophores into high macroscopic NLO activities of polymers, because of the strong dipole–dipole interactions among the chromophore moieties with donor–π-acceptor structure in the polymeric system. This interaction makes the poling-induced noncentrosymmetric alignment of chromophore moieties (necessary for the materials to exhibit the NLO effect) a daunting task during the poling process under an electric field.[11] Fortunately, according to the experimental results and theoretical analysis of Jen, Dalton, and co-workers, the dendritic structure, present in dendrimers, hyperbranched polymers, and dendronized polymers (in which some isolation groups were bonded to the chromophore moieties to decrease the interactions and increase the poling efficiency by applying the site isolation principle), was considered a very promising molecular topology for the next generation of highly efficient NLO materials and expected to meet the basic requirements of practical applications: large macroscopic optical nonlinearity, high physical and chemical stability, and good optical transparency.[12,13] On the basis of their excellent work, and according to the concept of "suitable isolation group" summarized from the experimental results of our systematically research in the dendronized polymers,[14,15] we recently designed a new convergent approach to NLO dendrimers **G1**–**G3** (Scheme S1 in the Supporting Information).[16] These dendrimers not only confirmed our thoughts on the formed triazole rings as the suitable isolation groups to enhance the macroscopic NLO effect, but, more excitingly, also demonstrated that accompanying the increased loading density of the chromophore moieties was an increase in the tested NLO effects. This result was really abnormal but very important to solve the obstacle in the NLO field mentioned above, and indicated that the frequently observed asymptotic dependence of electrooptic activity on the chromophore number density may be overcome through rational design.[17]

If the loading density of chromophore moieties in dendrimers is further increased, much better NLO effects should be achieved. Thus, we attempted to prepare high-generation dendrimers as derivatives of **G1**–**G3**. However, in this instance, the higher-generation dendrimers could not be obtained easily in satisfactory yields through the convergent method as **G1**–**G3**, because of steric effects and the difficulty of chromatographic separation. To improve the synthetic

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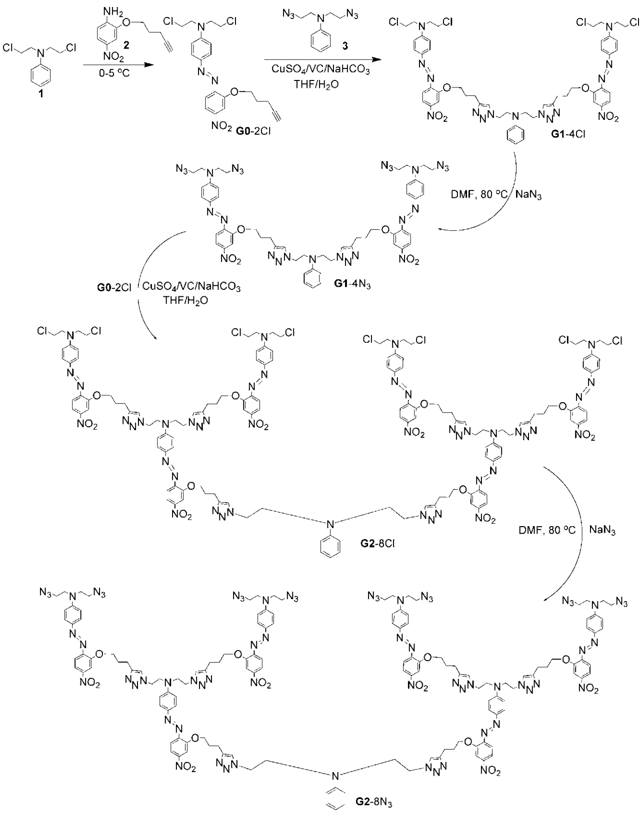
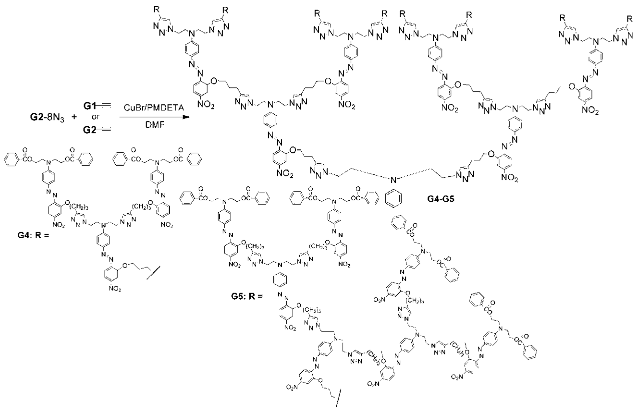
efficiency, a "double-stage" method was designed (Schemes 1 and 2), in which the core (**G2**–8 N_3, Scheme 1) was prepared through a divergent approach through click chemistry, while the end-capped dendrons (**G1**-≡ and **G2**-≡, Scheme S1) were obtained through a convergent approach also by click chemistry. By the combination of divergent and convergent approaches, as well as the usage of click chemistry, the whole synthetic route was convenient and highly efficient. Excitingly, accompanying the change in loading concentration of the chromophore moieties from 0.520 in **G3** to 0.537 in **G4** to 0.544 in **G5**, the measured NLO coefficient values increased from 122.7 (**G3**) to 177.0 (**G4**) to 193.1 pm V^{-1} (**G5**), which further confirmed that the frequently observed asymptotic dependence of electrooptic activity on the chromophore number density may be overcome through rational design. To the best of our knowledge, the tested NLO effect (193.1 pm V^{-1}) is the highest value reported so far for simple azo chromophore moieties. Thus, the successful examples might open up a new avenue to achieve further good NLO polymers with even higher NLO effects by utilizing other NLO chromophores with larger β values, and the "double-stage" method coupled with "click chemistry" could aid other scientists in the convenient preparation of further high-generation dendrimers with perfect structures.



Scheme 1. Synthesis of the core (**G2**–8 N_3) of the dendrimers.

As shown in Schemes 1 and 2, high-generation dendrimers **G4** and **G5**, bearing 30 and 62 NLO azobenzene chromophore moieties, respectively, were conveniently prepared in good yields. The success of the synthetic route should be ascribed to the nearly perfect Sharpless "click chemistry", as well as a well-designed "double-stage" approach. The core (**G2**–8 N_3) was synthesized through a divergent approach from AB_2-type monomer **G0**–2 Cl, which was crafted to contain two chloroethyl groups and one terminal alkyne group. After the click chemistry reaction between **G0**–2 Cl and compound **3**, the first-generation dendrimer **G1**–4 Cl was obtained easily in 75.7 % yield. Then, **G1**–4 N_3 was produced in high yield (99.0 %) through the substitution of the chloride groups in **G1**–4 Cl. A click reaction between the azides of **G1**–4 N_3 and the terminal alkyne in chromophore **G0**–2 Cl gave the second-generation dendrimer **G2**–8 Cl, which could undergo a further substitution reaction of the chloride groups to produce the core **G2**–8 N_3 in high yield (96.3 %). Therefore, it seemed that by repeating click reaction and substitution reaction, high-generation dendrimer **G5** would be obtained. However, unexpectedly, **G3**–16 Cl could not be synthesized successfully, although we tried several times, by using either $CuSO_4$/sodium ascorbate or CuBr/pentamethyldiethyltriamine (PMDETA) as catalyst. Moreover, even though the preparation of **G3**–16 Cl was successful, to synthesize the target dendrimer (**G5**), there were still five steps required (Route 1 in Table 1), which was very tedious and some other problems might be encountered.



Scheme 2. Synthesis of dendrimers **G4** and **G5**.

On the other hand, we have prepared a series of NLO dendrimers (**G1**–**G3**) through a convergent approach (Scheme S1 and Chart S1 in the Supporting Information). In

Table 1: Synthesis of **G5**. The number of the chromophore moieties in the dendrimers is given in parentheses.

Route 1:
G2-8N3 → G3-16Cl → G3-16N3 → G4-32Cl → G4-32N3 → G5

Route 2:
G2-≡ → G3 → G3-≡ → G4 → G4-≡ → G5

Route 3:
G2-8N3 + G2-≡ → G5

	G0-≡	**G1**-≡	**G2**-≡
G0–2 N_3	**G1**(2)	**G2**(6)	**G3**(14)
G1–4 N_3	**G2**(7)	**G3**(14)	**G4**(30)
G2–8 N_3	**G3**(14)	**G4**(30)	**G5**(62)

that synthetic route (convergent approach), we took advantage of the combination of click chemistry and azo coupling reaction to make all the involved reactions conducted under mild conditions, and there was no need to protect/deprotect some functional groups or include the conversion of one reactive group to another. In this route (Route 2 in Table 1), **G5** might also be obtained from **G3** with only four steps needed, which is relatively simple in comparison with Route 1. However, as mentioned above, the higher-generation dendrimers could not be obtained easily in satisfactory yields through the convergent method as for **G1**–**G3**, because of steric effects and the difficulty of chromatographic separation. The difficulty did not originate from the "click" reaction, but rather the introduction of terminal alkyne group by the azo coupling reaction. For example, in the synthesis of **G2**-≡, the yield was not higher than 62.8 %, even though the azo coupling reaction was conducted for 80 h, whereas the yields of **G0**-≡ and **G1**-≡ were 90.0 and 76.5 %, respectively. Thus, the yields of **G3**-≡ and **G4**-≡ in the next steps would be much lower. Also, with an increase in generation of the dendrimer, purification becomes much more difficult. Therefore, Route 2 would be more expensive and difficult to handle.

However, **G5** could be obtained through Route 3 (Table 1), which is a combination of Routes 1 and 2, as a product of the "click" reaction between **G2**–8 N_3 and **G2**-≡. Thus, by using this "double-stage" approach, the number of required synthetic steps could be decreased. The preparation of **G4** and **G5** proceeded to completion in less than 6 h as monitored by FTIR spectroscopy (disappearance of the peak centered at 2096 cm^{-1} associated with the azido groups). The purification of **G4** and **G5** was very simple: repeated precipitation of THF solutions into acetone, since **G2**–8 N_3, **G1**-≡, and **G2**-≡ are soluble in acetone. Satisfactory yields were obtained (75.8 % and 73.7 %, respectively), thanks to the powerful "click" reaction.

The reaction products were characterized by spectroscopic analysis, and all gave satisfactory data (some data listed in Table S1) corresponding to their expected molecular structures (see Figure S1–S16 in the Supporting Information). The degradation temperatures (T_d) for **G4** and **G5** were around 262 and 275 °C (Table 2), respectively, revealing that the dendrimers are thermally stable. Also, the growth of the NLO dendrimers caused an increase in their glass transition temperature (T_g). The T_g values of **G4** and **G5**—117 and 125 °C, respectively,—were higher than that of **G3** (90 °C).

Table 2: Physical and NLO data of the dendrimers.

	T_d [°C][a]	T_g [°C][b]	d_{33} [pm V^{-1}][c]	$d_{33(\infty)}$ [pm V^{-1}][d]	Φ[e]	N[f]
G1	300	56	100.0	13.4	0.20	0.402
G2	295	76	108.1	14.2	0.18	0.488
G3	278	90	122.7	18.2	0.25	0.520
G4	262	117	177.0	31.3	0.27	0.537
G5	275	125	193.1	34.1	0.31	0.544

[a] The 5% weight loss temperature of polymers detected by TGA analyses under nitrogen at a heating rate of 10 °C min^{-1}. [b] Glass transition temperature of polymers detected by the DSC analyses under argon at a heating rate of 10 °C min^{-1}. [c] SHG coefficient. [d] The nonresonant d_{33} values calculated by using the approximate two-level model. [e] Order parameter $\Phi = 1\ A_1/A_0$, where A_1 and A_0 are the absorbance of the polymer film after and before corona poling, respectively. [f] Loading density of the effective chromophore moieties.

G4 and **G5** were soluble in polar organic solvents, such as chloroform, THF, DMF, and DMSO. Similar to **G3**, **G4** and **G5** exhibited a good site-isolation effect in comparison with free chromophore molecules and low-generation dendrimers, revealing the fact that the exterior benzene moieties and the interior triazole rings surrounding the azo chromophore moieties play a key role in shielding them from the solvatochromic effect (Figure S17 and Table S2 in the Supporting Information). The maximum absorption wavelengths (λ_{max}) of **G4** and **G5** were nearly the same as that of **G3** in solution; however, in solid films, **G4** and **G5** exhibited blue-shifted maximum absorption (470 nm) relative to that of **G3** (480 nm), demonstrating the more perfect 3D structure of **G4** and **G5**. Thus, the enhanced effective site isolation achieved in **G4** and **G5** directly decreases the strong intermolecular dipole–dipole interactions among chromophore moieties and greatly benefits the ordered noncentrosymmetric alignment of the chromophore moieties during the poling process. In addition, the blue-shifted absorption maximum of dendrimers would result in wide optical transparency windows and contribute to practical applications in photonics fields.

G4 and **G5** exhibit good film-forming ability, and their poled films were prepared for the evaluation of their NLO activities. A convenient technique to study the second-order NLO activity was to investigate the second-harmonic generation (SHG) processes characterized by d_{33}, an SHG coefficient. The test procedure was similar to that we reported previously,[18] and from the experimental data, their d_{33} values were calculated at the 1064 nm fundamental wavelength (Table 2).

In our previous work, the d_{33} values increased from **G1** to **G3** (Table 2), accompanying the increasing loading density of the chromophore moieties. Here, upon the growth of NLO dendrimers to the four (**G4**) and fifth generation (**G5**), the loading density of chromophore moieties was increased further still, and their NLO effects were enhanced accordingly: accompanying the increase in loading concentration of the chromophore moieties from 0.520 in **G3** to 0.537 in **G4**, to 0.544 in **G5**, the measured NLO coefficient values increased from 122.7 (**G3**) to 177.0 (**G4**), to 193.1 pm V^{-1} (**G5**). These values are very high relative to those of other reported NLO polymers containing nitroazobenzene chromophores. These encouraging results should be ascribed to the more perfect 3D structure of **G4** and **G5** as discussed above. Furthermore, the exterior benzene moieties and the interior triazole rings played an important role in decreasing the interactions and enhancing the poling efficiency, according to the concept of "suitable isolation group".[14,15] As there might be some resonant enhancement due to the absorption of the chromophore moieties at 532 nm, the NLO properties of dendrimers should be smaller, as shown in Table 2 ($d_{33}(\infty)$). Because of their wide optical transparency window (the maximum absorption wavelengths of their films were only around 470 nm), as well as their large d_{33} values, the $d_{33}(\infty)$ values of

G4 and **G5** were still very high (31.3 and 34.1 pm$\,$V^{-1}), thus making them attractive for potential optics applications.

It should be pointed out that although the loading density of the chromophore moieties increased by only 0.017 from **G3** to **G4**, the d_{33} value was enhanced by 55 pm$\,$V^{-1}, but only by about 14 pm$\,$V^{-1} from **G2** to **G3**, despite the increase in loading density of 0.032. From **G4** to **G5**, the loading density increased by only 0.007, but the d_{33} value was still enhanced by 16 pm$\,$V^{-1}. This result might indicate that after the loading density of the chromophore moieties increased beyond a critical point, the NLO effect would be enhanced dramatically with further increases in loading density. While further research is still needed, our results demonstrate that accompanying the increasing of the loading density of the chromophore moieties, the tested NLO effects increase, indicating that the frequently observed asymptotic dependence of electrooptical activity on chromophore number density may be overcome through rational design, in accordance with the results and prediction of Sullivan, Robinson, Dalton, and coworkers.[17] Thus, our results could provide some useful information for the rational design of NLO materials with better performance.

To further explore the alignment of the chromophore moieties in these dendrimers, we measured their order parameter (Φ, see Table 2 and Figure S18). The Φ values of **G4** and **G5** were calculated (see footnote [e] in Table 2 for equation) to be 0.27 and 0.31, respectively, confirming that the alignment of the chromophore moieties in **G4** and **G5** upon poling becomes easier than that in **G3** ($\Phi = 0.25$). Another interesting phenomenon was that accompanying the enhancement of d_{33} values, the best poling temperatures of **G4** and **G5** also increased relative to that of **G3**, indicating that better temporal stabilities of the SHG signals could be realized.

Depoling experiments of **G3**–**G5** were conducted, whereby the real-time decays of the SHG signals were monitored as the poled films were heated from 35 to 140 °C in air at a rate of 4 °C$\,$min^{-1}. Figure 1 shows the decay of the SHG coefficient of **G3**–**G5** as a function of temperature. **G3** decays at a temperature of only 70 °C, whereas the decay temperatures of **G4** and **G5** increased to 100 and 107 °C, respectively. This result was unexpected, since no crosslinkable groups were introduced. Thus, it could be attributable to the 3D macromolecule architecture, which might suppress the relaxation of the ordered dipole alignment to some extent. Thus, coupled with their large NLO effects and improved optical transparency, **G4** and **G5** are promising candidates for practical NLO applications.

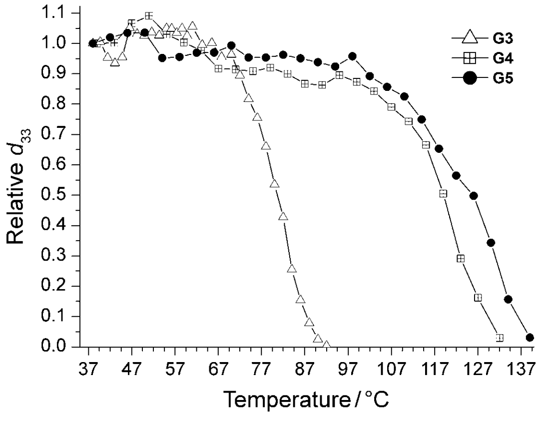


Figure 1. Decay curves for the SHG coefficient d_{33} of **G3**–**G5** as a function of temperature.

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