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# Nonlinear Optical Dendrimers from Click Chemistry: Convenient Synthesis, New Function of the Formed Triazole Rings, and Enhanced NLO Effects

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The use of 1,3-dipolar cycloaddition reactions between azides and alkynes (click chemistry), also termed the Sharpless "click" reaction, has aroused much interest among researchers because of its remarkable features such as nearly quantitative yields, mild reaction conditions, broad tolerance toward functional groups, low susceptibility to side reactions, and simple product isolation.[1] And it has been extremely successful as a versatile synthetic tool to construct novel polymeric systems varying from block copolymers, star polymers, dendrimers, to complex macromolecular structures.[2−11] However, the new formed triazole rings during the click chemistry reaction were nearly ignored, and their possible functions attract less attention.[12]

On the other hand, 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, THz wave generation and detection, and many other applications.[13−17] It is well-known that second-order NLO properties originate from the noncentrosymmetric alignment of NLO chromophores (generally achieved under an electric field), either doped as a guest or covalently introduced to the polymer systems, although the strong intermolecular dipole−dipole interactions among the chromophore moieties in the polymeric system make the poling-induced noncentrosymmetric alignment of chromophores a daunting task.[18] Fortunately, according to the experimental results and theoretical analysis, the dendritic structure, present in dendrimers, hyperbranched polymers, and dendronized polymers,[18−20] in which some isolation groups are bonded to the chromophore moieties to decrease the interactions and increase the poling efficiency by utilization of the site isolation principle,[21] is considered as 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. However, the utilization of click chemistry for the construction of NLO materials with dendritic structure is still very scarce, and there are no reports concerning the NLO dendrimers, no matter the synthetic convenience brought by the click chemistry proved in other polymeric systems and the largely enhanced NLO effect resulted from the cone shape of dendrimers,[22] possibly due to the synthesis difficulty or lack of a rational synthetic approach.

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Recently, we have demonstrated in the dendronized polymers that the macroscopic nonlinearity of NLO polymers could be boosted several times higher by bonding "suitable isolation groups" to the NLO chromophore moieties (Charts S1−S6).[23] On the basis of our systematically research on "the suitable isolation group",[24] it is expected that if more isolation groups, but not only one group as in **P1**−**28**, are introduced to one chromophore group, the bulk of the isolation spacer should be smaller. Thus, we consider that the above-mentioned triazole one might possibly act as suitable isolation groups if carefully designed. Therefore, with the aim to develop NLO dendrimers with good performance from click chemistry and broaden our research from NLO dendronized polymers to dendrimers, we designed a new synthetic approach to NLO dendrimers (Scheme 1), with the combination of the click chemistry and azo coupling reaction, based on our previous work.[25] All the dendrimers were conveniently obtained, well characterized, and demonstrate good dendritic structure, blue-shifted absorption, and much enhanced NLO performance.

The whole synthetic route is shown in Scheme 1, and the detailed preparation procedure is described in the Supporting Information. Compound **1** was prepared as reported previously,[24d] and the followed ester reaction at room temperature gave **G0-**≡, which reacted with compound **2** via click reaction under room temperature to yield **G1**. Then, through the efficient azo coupling reaction at 0 °C, another constructing block of chromophore group with push−pull structure was formed, resulting in three chromophore moieties in **G1-**≡, in comparison with two in **G1**. Simultaneously, one reactive alkyne group was introduced for the further growing of the dendrimers. Repeating the click reaction, and then azo coupling reaction, **G1-**≡ could be easily converted to **G2** and then **G2-**≡. And through another click reaction, **G3**, which totally contains 14 chromophore moieties, was obtained in good isolated yield (69.8%). It should be pointed out that the azo coupling reaction was undergone in pure organic solvent, avoiding the general used inorganic acids and the possible low solubility of the reaction starting materials in the mixed solvents of organic solvent and water under the normal azo coupling reactions. The isolated yield of **G1** is as high as 97.5%, while those of others are around 70% (Table 1). This is reasonable: as mentioned above, all the NLO chromophore moieties possess high polar push−pull structure and could be easily absorbed on the gel column during the purification process, directly leading to the reduced isolation yields once the number of chromophore moieties in one dendrimer molecule increases. Thus, all the involved reactions are conducted under very mild conditions, and the efficiency of this synthetic approach is very high, no need to protect/deprotect some functional groups or include the converting process from one reactive group to another. So, the successful examples of these NLO dendrimers exhibit the flexible synthetic power with the combination of two efficient chemical reactions and might give light on the syntheses of other functional dendrimers from more economic preparation routes. It is easy seen that the whole synthetic method is a convergent growth approach, not the general used divergent strategy for NLO dendrimers, thus providing for more exact macromolecular architectures with nearly no defects, greater monodispersity, and easy purifications.

The reaction products are well characterized by spectroscopic analyses, and all give satisfactory data (some data listed in Table 1) corresponding to their expected molecular structures

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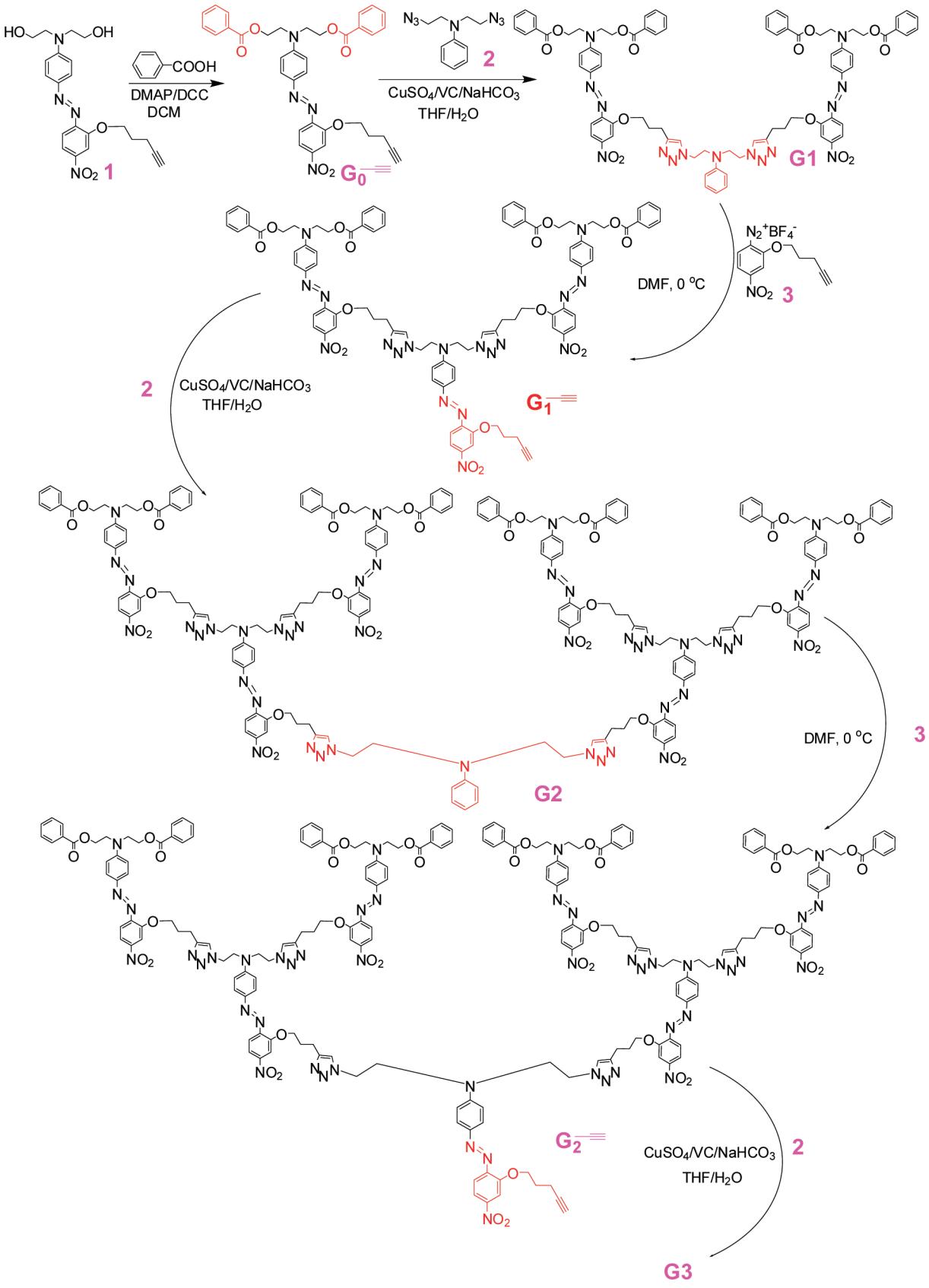
**Scheme 1. Synthesis of NLO Dendrimers**




(see Supporting Information for details). As shown in their IR spectra (Figures S1 and S2), there are weak stretching vibrations of the ≡C−H bonds at about 3300 $cm^{-1}$ in **G0-≡**, **G1-≡**, and **G2-≡**; however, after the click reaction, these absorption bands disappear and cannot be found in **G1**, **G2**, and **G3**. This phenomenon is further confirmed by the presence and absence of the signal of the phenyl proton at the para position to the amino group in the benzene ring at about

**Table 1. Characterization Data of Dendrimers**

| no. | yield (%) | $M_w$[a] | $M_w/M_n$[a] | $m/z$[b] | $m/z$ (calcd) |
|---|---|---|---|---|---|
| **G1** | 97.5 | 1675 | 1.02 | 1472.6 | 1472.6[c] |
| **G1-≡** | 76.5 | 1979 | 1.03 | 1703.4 | 1703.6[c] |
| **G2** | 72.6 | 3760 | 1.05 | 3661.9 | 3661.8[d] |
| **G2-≡** | 62.8 | 4132 | 1.02 | 3893.2 | 3893.0[d] |
| **G3** | 69.8 | 6676 | 1.05 | 7994.0 | 7994.3[d] |

[a] Determined by GPC in THF on the basis of a polystyrene calibration. [b] Measured by MALDI-TOF mass spectroscopy. [c] Calculated for $[M + H]^+$. [d] Calculated for $[M + Na]^+$.

**Table 2. Maximum Absorption of Dendrimers ($\lambda_{max}$, nm)[a]**

| | THF | [a] | [b] | [c] | DMF | DMSO |
|---|---|---|---|---|---|---|
| **G1** | 462 | 460 | 461 | 465 | 476 | 491 |
| **G2** | 462 | 457 | 456 | 460 | 474 | 485 |
| **G3** | 459 | 454 | 455 | 453 | 472 | 478 |

[a] [a] 1,4-Dioxane. [b] Chloroform. [c] Dichloromethane. The maximum absorption wavelength of dendronized chromophores solutions with the concentrations fixed at 0.01 mg/mL.

**Table 3. Physical and NLO Results of Dendrimers and Polymers**

| no. | $T_g$[a] (°C) | $T_d$[b] (°C) | $T_e$[c] (°C) | $d_{33}$[d] (pm/V) | $\Phi$[e] | $N$[f] |
|---|---|---|---|---|---|---|
| **G1** | 56 | 300 | 52 | 100.0 | 0.20 | 0.402 |
| **G2** | 76 | 295 | 86 | 108.1 | 0.18 | 0.488 |
| **G3** | 90 | 278 | 102 | 122.7 | 0.25 | 0.520 |

[a] Glass transition temperature ($T_g$) of polymers detected by the DSC analyses under argon at a heating rate of 10 °C/min. [b] The 5% weight loss temperature of polymers detected by the TGA analyses under nitrogen at a heating rate of 10 °C/min. [c] The best poling temperature. [d] Second harmonic generation (SHG) coefficient. [e] Order parameter $\Phi = 1 - A_1/A_0$; $A_1$ and $A_0$ are the absorbance of the polymer film after and before corona poling, respectively. [f] The loading density of the effective chromophore moieties.

6.7 ppm before (in **G1**, **G2**, and **G3**) and after (in **G0-≡**, **G1-≡**, and **G2-≡**) the azo coupling reactions in their $^1$H NMR spectra (Figures S3−S8).

Moreover, as the ratios of the nitro groups to the carbonyl ones increase, accompanying the growth of the NLO dendrimers from first generation to the third, the absorption intensity of the nitro groups becomes more and more stronger, in comparison with that of the carbonyl ones. Gel permeation chromatography (GPC) is utilized for the analysis of the dendrimer growth, and the tested molecular weights become larger step by step upon the growth of NLO dendrimers. Excitingly, very sharp peaks are observed for all the dendrimers in the GPC results (Figure S9), indicating the absence of impurity and the dendritic architectures with nearly no defects. In addition to accurately show the exact molecular weights of these NLO dendrimers, the MALDI-TOF mass study also proves this point, since almost only one peak is seen in their spectra (Figures S10−S14).

All the NLO dendrimers are soluble in common organic solvents, such as chloroform, THF, DMF, and DMSO. The UV−vis absorption spectra are shown in Figures S15−S20, and the maximum absorption wavelengths for the $\pi-\pi^*$ transition of the azo moieties in them are listed in Table 2. It is easily seen that from the first generation dendrimer (**G1**) to the third one (**G3**) the maximum absorption wavelength blue shifts up to 13 nm (**G1** and **G3** in DMSO) in different organic solvents. And the difference of the same dendrimer in different solvents is also different; for example, the maximum absorption of **G1** is 462 nm in THF, but 491 nm in DMSO (29 nm red-shifted), while those of **G3** are 459 and 478 nm (only 19 nm red-shifted), respectively. The phenomena are ascribed to the site-isolation effect,[26] revealing the fact that the isolation moieties (triazole groups) surrounding the azo chromophore moieties play a key role to shield them from the solvatochromic effect upon the growth of the NLO dendrimers. The achieved site isolation effect would benefit the NLO effect of the NLO dendrimers by reducing the aggregation of the azo chromophore moieties no matter in solution or solid state. Also, the blue-shifted maximum absorption in **G3** will surely result in its wide optical transparency window and contribute to the practical application of these dendrimers.

The growth of the NLO dendrimers also causes the increasing of the glass transition temperature ($T_g$), as observed by DSC measurement (Table 3). The $T_g$ increases from the first generation (**G1**), 56 °C, to the second generation (**G2**), 76 °C, and then further increased to the third generation (**G3**), 90 °C (Figure S21). The NLO dendrimers are thermally stable, nearly no apparent weight loss observed blow 200 °C. Their TGA thermograms are shown in Figure S22, and the 5% weight loss temperature decreases upon the increasing of the generation number, which is possibly due to the increasing of the loading density of the effective chromophore moieties in the dendrimers.

The NLO activities of the dendrimers are measured similarly as reported previously,[23] and from the experimental data, their $d_{33}$ values are calculated at the 1064 nm fundamental wavelength (Table 3). It should be pointed out that all the dendrimers can be easily handled to prepare their thin films by spin-coating, demonstrating their good processability. The NLO effects are much higher than our other NLO polymers carrying similar azobenzene chromophores including those with suitable isolation groups; this should be ascribed to the dendritic structure of these NLO dendrimers and good isolation effect of triazole and benzoic groups. From the first generation (**G1**) to the third one (**G3**), the tested NLO values increase more than 20%, partially proving the more apparent effective site isolation effect. Upon the growth of the NLO dendrimers, the loading density of the effective chromophore moieties increases accordingly. In our case, the density is raised from 0.402 of **G1** to as high as 0.520 in **G3**, which really possesses very high loading density of effective chromophore moieties. It is well-known that in theory,[27] under identical experimental conditions, $d_{33}$ is proportional to the density of the chromophore moieties (eq S1); however, due to the significantly higher chromophore−chromophore electrostatic interaction, the relationship between the chromophore density and the NLO effect is not linear any longer, and there is a maximum value of NLO effect at a special concentration of the chromophore moieties. Further increasing the loading level of chromophore moieties can only decrease the NLO effect. By the introduction of isolation spacers according to the site isolation principle, the loading density of the chromophore moieties could be dramatically increased before the maximum NLO value achieved; however, there is still a critical point, and the relationship is not linear. Here, the loading density increases upon the growth of NLO dendrimers; correspondingly, the tested NLO effect becomes larger, demonstrating a deviation from the dipolar frustration that typically limits the NLO effect in conventional chromophore/polymer composite materials. The tested order parameter ($\Phi$) of the NLO dendrimers (Figures S23−S25) also confirms that the alignment of the chromophore moieties under electric field poling becomes easier, accompanying the growth of the generation number. This indicates that triazole groups gradually act as good isolation groups to minimize the strong intermolecular dipole−dipole interactions among the chromophore moieties upon the growth of the NLO dendrimers, realizing our thought of the utilization of triazole rings as good isolation spacers and well in accordance with the obtained results from their UV−vis spectra as discussed above. Combined with the recent work of Sullivan, Robinson, and Dalton and their prediction,[28] this exciting phenomenon also discloses that by choosing suitable isolation spacers and through rational design, it is possible to

experimentally realize the linear relationship between the loading density of chromophore moieties and the electro-optical activity.

In conclusion, we have reported herein the efficient synthesis of **G1**−**G3** NLO dendrimers from the click chemistry reaction. The preliminary results demonstrated that:

1. The Sharpless "click" reaction could be used for the construction of NLO dendrimers with good performance.

2. Not only the click chemistry reaction itself provides the convenient synthesis of NLO dendrimers, but also the formed triazole rings in the reaction is utilized to act as good isolation groups at the very beginning of dendrimer design. By the further modification, the function of the triazole rings might be brought into full play.

3. Accompanying the increasing of the loading density of the chromophore moieties, the tested NLO effects are going higher, partially proving the prediction of Dalton et al. and indicating that the frequently observed asymptotic dependence of electro-optic activity on chromophore number density may be overcome through rational design.

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**Supporting Information Available:** Structure of some NLO polymers; synthetic details of all the dendrimers; IR, NMR, DSC, TGA, and MALDI-TOF spectra; UV−vis spectra of the polymer films. This material is available free of charge via the Internet at http://pubs.acs.org.

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