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High-Generation Second-Order Nonlinear Optical (NLO) Dendrimers that Contain Isolation Chromophores: Convenient Synthesis by Using Click Chemistry and their Increased NLO Effects

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Abstract: Herein, high-generation dendrimers **G4-NS** and **G5-NS**, which contained 30 and 62 azo-benzene chromophore moieties, respectively, were conveniently prepared in high purity and satisfied yields by a combination of divergent and convergent approaches, coupled with the utilization of the powerful Sharpless click reaction. These dendrimers possessed a regular structure of alternating layers of nitro-based and sulfonyl-based azo chromophores in which the sulfonyl-based azo-chromophore moieties were utilized as co-isolation groups for the nitro-based moieties to achieve larger macroscopic second-order nonlinear optical (NLO) effects. These high-generation dendrimers (**G4-NS** and **G5-NS**) displayed very large NLO efficiencies (up to 253.0 pm V^{-1}), which is, to the best of our knowledge, the record highest efficiency for simple azo-chromophore moieties.

Keywords: azo compounds · chromophores · click chemistry · dendrimers · nonlinear optics

Introduction

Dendrimers are defect-free and perfectly monodisperse macromolecules with regular and highly branched 3D structures; their structure can be easily controlled by changing the core, dendron, or the periphery, thereby conveniently allowing for the design of new multifunctional molecules. For examples, core- or terminal-modified-,[1] layered-,[2] segmented-,[1a,2a,3] and tailored-type[4] dendrimers have been reported for various applications. Moreover, their special 3D global highly branched structure can lead to some special properties, including nanometer size, multivalent character, the modularity of their assembly, high solubility, and low viscosity, which make them competitive candidates for applications in a variety of fields, including catalysis, biology, and materials science.[1–5]

In the field of materials science, the development of organic NLO materials is motivated by their promising performance and lower cost for applications in telecommunications, computing, embedded-network sensing, terahertz-wave generation and detection, etc.[6] One major obstacle that hinders the rapid development of this field is the efficient translation of the large $\mu\beta$ values of organic chromophores into high macroscopic NLO activities of the polymers because of the strong dipole–dipole interactions between the chromophore moieties and the donor–π–acceptor structure in the polymeric system. These interactions make the poling-induced noncentrosymmetric alignment of chromophore moieties (which are necessary for the materials to exhibit the NLO effect) a daunting task during the poling process under an electric field.[7] According to the experimental results and theoretical analysis of Jen, Dalton, and co-workers, the dendritic structure that is present in dendrimers, hyperbranched polymers, and dendronized polymers (in which some isolation groups are bonded to the chromophore moieties to decrease the interactions between the chromophore moieties and increase the poling efficiency by applying the site-isolation principle) is considered to be a very promising molecular topology for the next generation of highly efficient NLO materials, which are expected to meet the basic requirements of practical applications: large macroscopic optical nonlinearity, high physical and chemical stability, and good optical transparency.[8] In particular, NLO dendrimers are ideal structures to explore the structure–property relationships.

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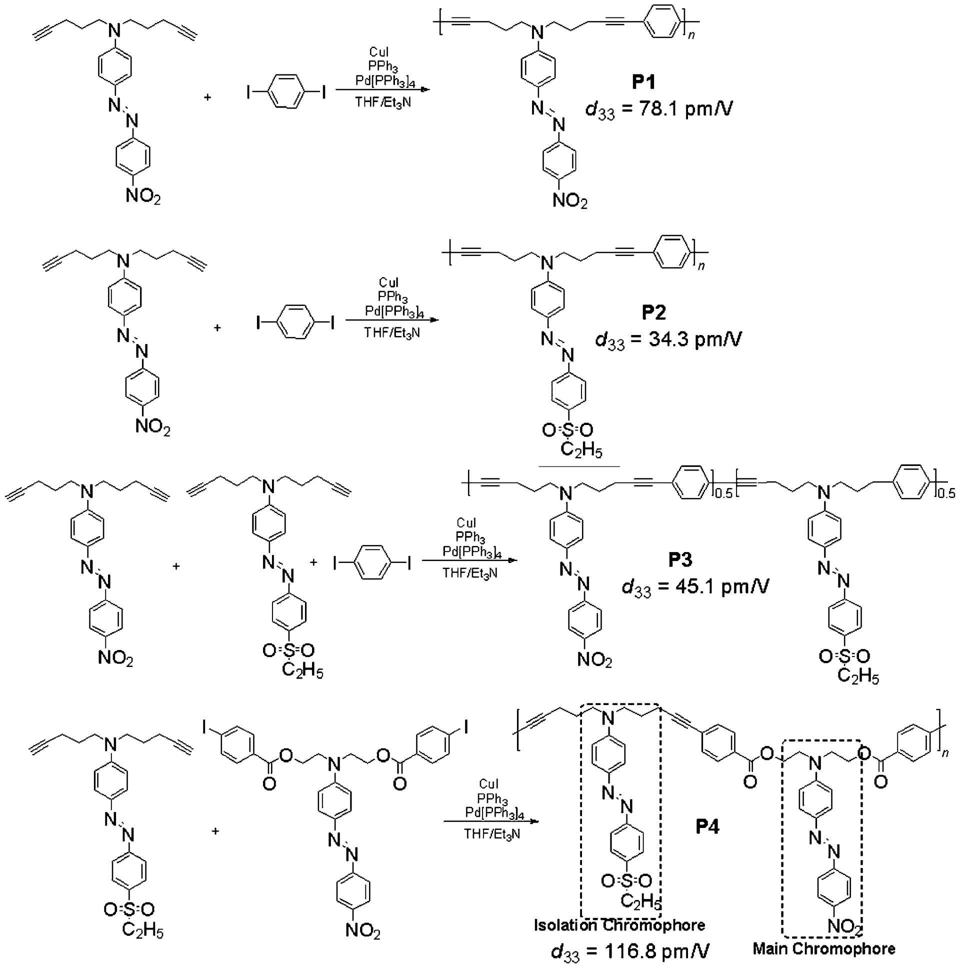
Based on the pioneering work of scientists in the field of NLO,[6–8] we have demonstrated that, in the dendronized polymers, the macroscopic nonlinearity of the NLO polymers could be boosted several times by bonding "suitable isolation groups" onto the chromophore moieties (see the Supporting Information, Charts S1–S6).[9] By applying this concept of "suitable isolation groups" to dendrimers, we recently prepared a new series of NLO dendrimers (**G1**–**G5**) through a convergent approach or the combination of divergent and convergent approaches[9h,i] (a "double-stage" method) by using click-chemistry reactions (see the Supporting Information, Schemes S1–S3).[10] These dendrimers not only confirmed our theory that the formed triazole rings are suitable isolation groups for enhancing the macroscopic NLO effect but also, more excitingly, they also demonstrated that, on increasing the loading density of the chromophore moieties, the NLO effects increased and the d_{33} value of **G5** was up to 193.1 pm V^{-1}, which was the highest value reported at that time for simple azo-chromophore moieties, thus indicating that the frequently observed asymptotic dependence of EO activity on chromophore density may be overcome through rational design, in accordance with the prediction of Sullivan, Robinson, Dalton, and co-workers.[11]

However, additional study was still needed to check this abnormal increase in the macroscopic NLO effect on increasing the loading density of the chromophore moieties in the dendrimers and to confirm the reproducibility and reliability of the "double-stage" method for the formation of high-generation dendrimers, such as **G4** and **G5** (see the Supporting Information, Scheme S3) by using Cu^{I}-catalyzed click chemistry.



Scheme 1. Synthesis of polymers **P1**–**P4** and their corresponding d_{33} values.

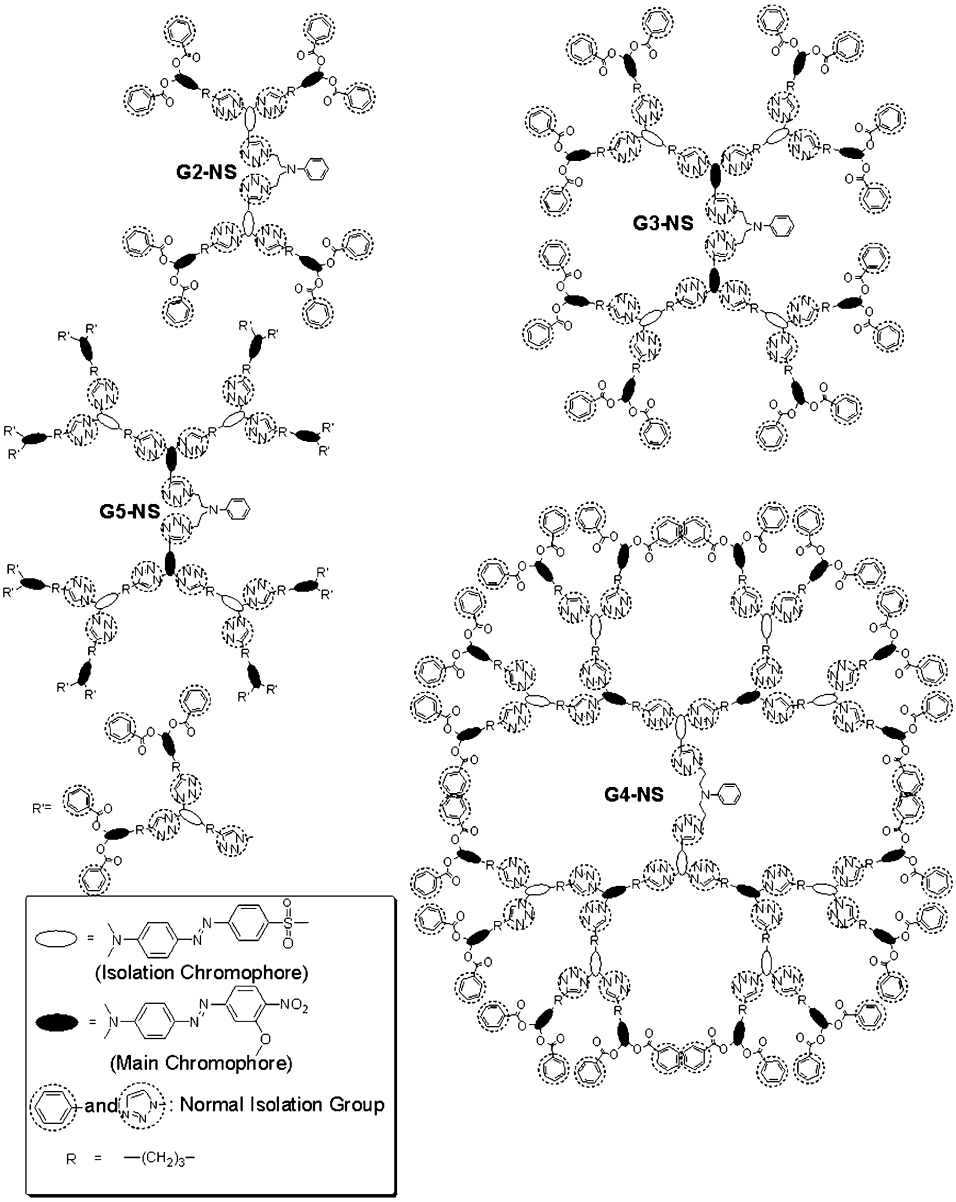
One the other hand, in all of our previous studies, the isolation groups were non-polar groups to impede the strong interactions between the chromophore moieties and they did not directly contribute to the macroscopic NLO effect but rather decreased the effective concentration of the NLO chromophore moieties. Thus, we wanted to consider using one chromophore with a lower $\mu\beta$ value as an isolation group for another chromophore group with a higher $\mu\beta$ value to achieve a high poling efficiency owing to the decreased strong electronic interactions. If this postulation was successful, the macroscopic NLO effect should be further enhanced. To answer this question, structure **P4**, which was constructed from two different chromophore moieties with the regular AB structure (Scheme 1), was obtained by using Sonogashira coupling reactions. For comparison, structures **P1**–**P3** (Scheme 1) were also prepared (for the synthesis and characterization data, see the Supporting Information). As shown in Scheme 1, structure **P4** exhibited the highest d_{33} value (116.8 pm V^{-1}), whilst the d_{33} value of its analogue, **P3**, which had an irregular structure, was only 45.1 pm V^{-1} (between the values of structures **P1** and **P2**). This result indicated that the sulfonyl-based chromophore (**C2**) could act as an effective isolation group for the nitro-based chromophore (**C3**), the main chromophore moiety, but only in the case of compound **P4**, which had a regular AB structure.

As mentioned above, one of the advantages of dendrimers is their controllable, perfect structure. Thus, considering this interesting result for compound **P4** and the abnormal increase in the macroscopic NLO effects of **G1**–**G5**, we wondered what would happen if these two chromophores were used to construct dendrimers with a regular structure that was similar to compound **P4** in which the formed triazole rings acted as “the suitable isolation group”, as in the case of structures **G1–G5**. Perhaps, much-better NLO effects could be achieved.

Thus, we attempted to design a new series of high-generation dendrimers (Scheme 2) in which two different chromophores (sulfonyl- and nitro-based chromophores) were arranging orderly. To improve the efficiency of the synthesis, the “double-stage” method that was used in the preparation of structures **G1–G5** was rational designed; by using this method, end-capped dendrons **G1-≡-NS** and **G2-≡-NS** (Scheme 3) were prepared through a convergent click-chemistry approach, whilst core structures **G1–4 N$_3$-S** (Scheme 4) and **G2–8 N$_3$-NS** (Scheme 5) were obtained through a divergent click-chemistry approach. Excitingly, the d_{33} value of **G5-NS** was 253.0 pm V^{-1}, which is the record highest value reported so far for simple azo-chromophore moieties. Herein, we report the synthesis, characterization, and properties of these new dendrimers.

Results and Discussion

Synthesis: As shown in Scheme 1, Scheme 3, Scheme 4, and Table 1, the dendrimers were conveniently prepared in good yields. The success of this synthetic route should be ascribed to the use of click-chemistry, which afforded the products in near-quantitative yield, as well as to the well-designed “double-stage” approach. The end-capped dendrons (**G2-≡-NS**, Scheme 3) were synthesized through a convergent click-chemistry approach that was similar to the synthetic route to **G2-≡** (see the Supporting Information, Scheme S1): First, **G1-≡-NS** was prepared from an efficient azo-coupling reaction between **G1-N** and diazonium fluoroborate **2** at 0 °C and another chromophore group that contained different acceptors (sulfonyl groups) was formed. Meanwhile, one reactive alkyne group was introduced for the further growth of the dendrimers. **G1-≡-NS** was converted into **G2-NS** by undergoing a click reaction with *N*,*N*-bis(2-azidoethyl)aniline (**1**) at room temperature. Simply repeating the azo-coupling reaction by using the nitro group as the electron acceptor readily afforded **G2-≡-NS** from **G2-NS**. This convergent synthetic route took full advantage of the combination of click chemistry and azo-coupling reactions and all of the reactions were conducted under mild conditions; moreover, there were no need to protect/deprotect some functional groups or to include conversion steps from one reactive group into another. By using this route, higher-generation dendrimers might be obtained. However, owing to steric effects and difficulties in chromatographic separation, they could not be easily obtained by using the convergent method as lower-generation dendrimers. As mentioned in our previous work,[10b] this difficulty did not originate from the click reaction, but instead from the introduction of terminal alkyne



Scheme 2. Structures of dendrimers **G2-NS–G5-NS**.

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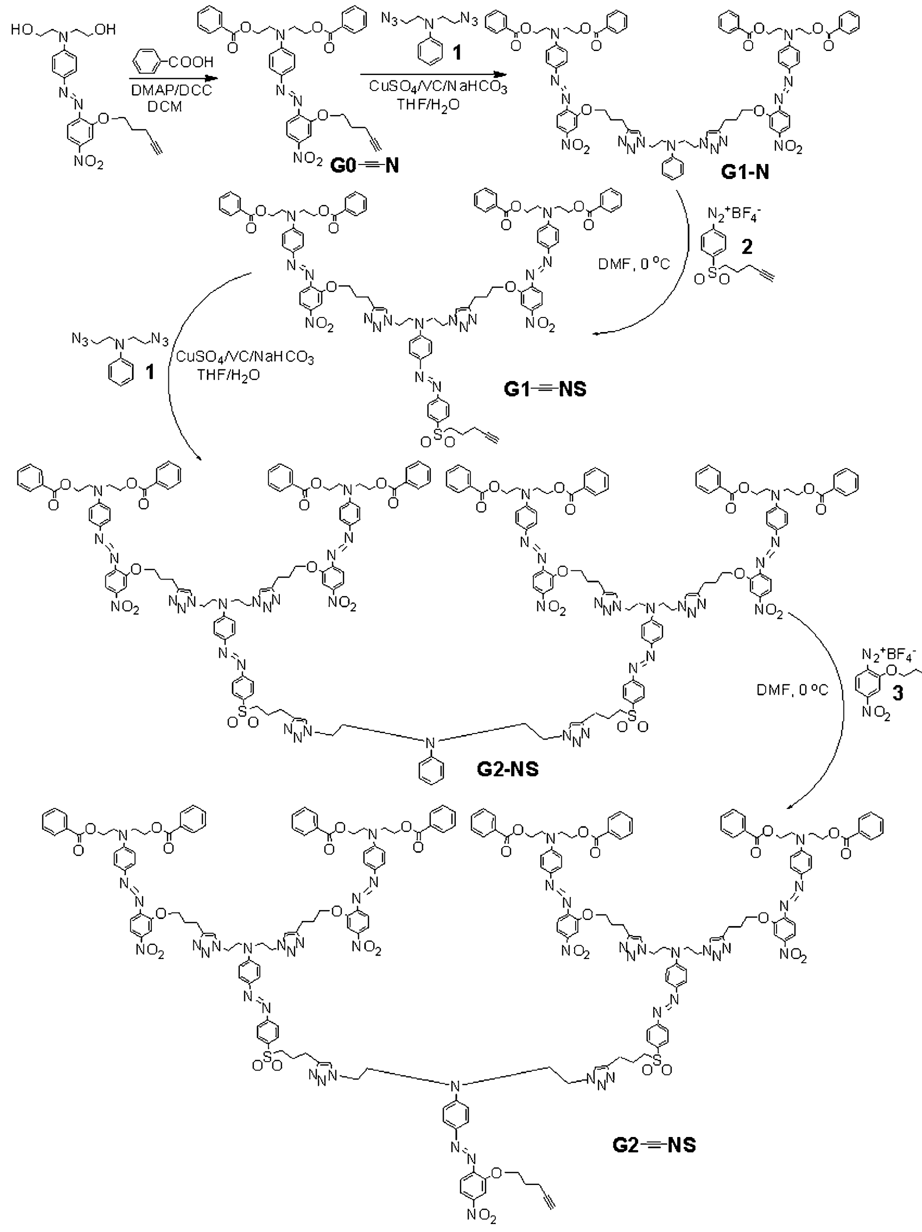


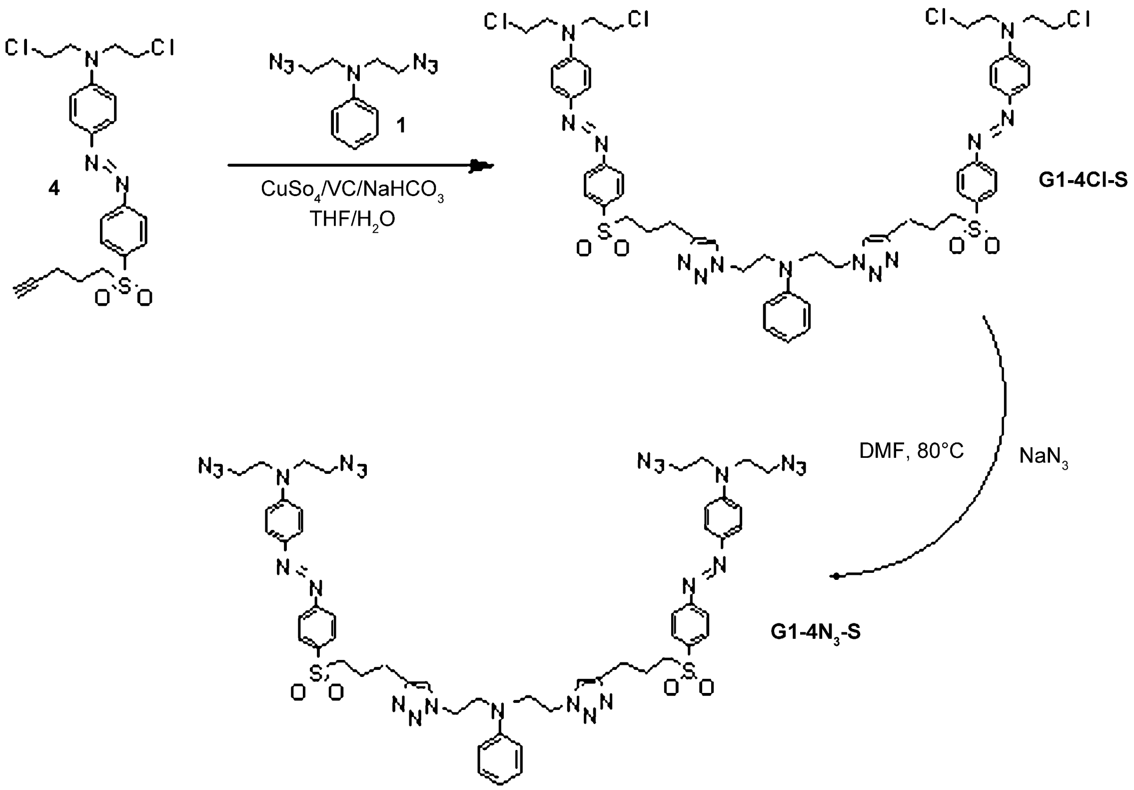
Scheme 3. Synthesis of end-capped dendrons **G1-≡-NS** and **G2-≡-NS**.

groups through the azo-coupling reaction. For example, in the synthesis of **G2-≡-NS**, the yield was not higher than 71.5 %, although the reaction was performed for 5 days, whilst the yield of **G1-≡-NS** was 89.1 %. Thus, the yields of **G3-≡-NS** and **G4-≡-NS** in the next steps would be much lower. Also, with increasing the number of generations, the purification became much-more difficult. Thus, another route that involved a divergent approach was designed.

All of the cores (**G1–4N$_3$-S** and **G2–8N$_3$-NS**) were prepared from AB$_2$-type monomers **4** or **5**, which contained two chloroethyl groups and one terminal alkyne group (Scheme 4 and Scheme 5). Herein, we will take the synthesis of **G2–8N$_3$-NS** as an example: After the click-chemistry reaction between compounds **5** and **1**, the first-generation dendrimer of **G1–4Cl-N** was obtained in 75.7 % yield and substitution of the chloride groups in **G1–4Cl-N** produced **G1–4N$_3$-N** (99.0 % yield). Next, the click reaction between the azide groups of **G1–4N$_3$** and the terminal alkyne group in chromophore **4** gave the second-generation dendrimer of **G2–8Cl-NS**, which could further undergo a substitution reaction of the chloride groups to produce the core of **G2–8N$_3$-NS** (88.4 % yield).

We were very excited to find that high-generation dendrimers could be obtained by using this "double-stage" approach (Table 1). The preparation of **G3-NS**, **G4-NS**, and **G5-NS** proceeded to completion in about 6 h, as monitored by FTIR spectroscopy (as determined by the disappearance of the peak that was centered at 2096 cm^{-1}, which was associated with the azido groups). **G3-NS** could still be purified by column chromatography on silica gel, whilst **G4-NS** and **G5-NS** were obtained by repeated precipitation of their solutions in DMF with acetone, because **G2-≡-NS**, **G1–4N$_3$-S** and **G2–8N$_3$-NS** were highly soluble in acetone. Thanks to the powerful click-chemistry reaction, their yields were satisfactory (84.0, 72.0, and 77.6 %, respectively).

Characterization: The products were well-characterized by spectroscopic analysis and they all gave satisfactory data (see the Experimental Section and the Supporting Information, Table S1) in accordance with their expected molecular structures (for details, see the Supporting Information, Figures S5–S35). The Supporting Information, Figures S5–S7 show the IR spectra of the new dendrimers. All of the dendrimers showed absorption bands that were associated with nitro groups (about 1520 and 1340 cm^{-1}), sulfonyl groups (about 1130 cm^{-1}), or the both. From the IR spectra of **G1-≡-NS** and **G2-≡-NS**, there was an absorption band that was derived from the C≡C-H stretching vibrations at about 3289 cm^{-1}, whereas this band disappeared in the spectra of **G2-NS**, **G3-NS**, **G4-NS**, and **G5-NS**. Compared with the spectra of **G1–4Cl-S** and **G2–8Cl-NS**, there was a new peak

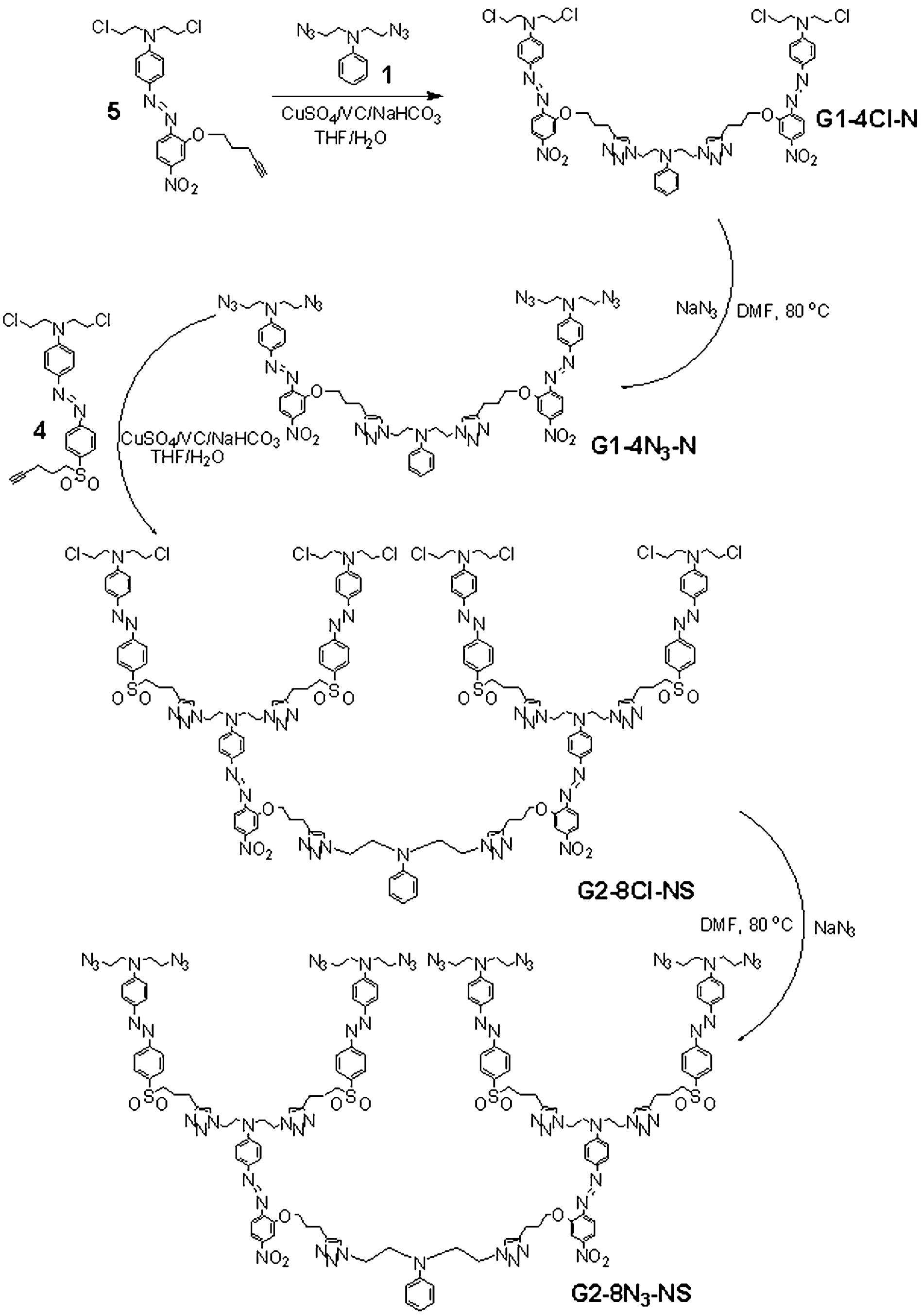


Scheme 4. Synthesis of the **G1-4N$_3$-S** dendrimer core.

at about 2095 cm^{-1}, which was associated with the azido groups in the IR spectra of **G1–4N$_3$-S** and **G2–8N$_3$-NS**, thus indicating that the nucleophilic-substitution reaction was successful. Moreover, the peak that was associated with the azido groups disappeared in the spectra of **G4-NS** and **G5-NS**, coupled with the appearance of a signal that was due to the carbonyl group at 1720 cm^{-1}, which showed that **G4-NS** and **G5-NS** were successfully prepared from the end-capping reactions of **G1–4N$_3$-S** and **G2–8N$_3$-NS**.

NMR spectroscopy was an especially useful tool for illustrating the growth of each new generation of dendrimer; all of the ^{1}H and ^{13}C NMR spectra are shown in the Supporting Information, Figures S8–S25. The presence and absence of the signal for the phenyl proton at the position *para* to the amino group in the benzene ring ($\delta \approx 6.7$ ppm) before (in **G2-NS** and **G3-NS** and even in **G4-NS** and **G5-NS**) and after the azo-coupling reactions (in **G1-≡-NS** and **G2-≡-NS**) in their ^{1}H NMR spectra, respectively, showed that their corresponding reactions were successful. The successful formation of **G1–4Cl-S** was confirmed by the appearance of a signal that corresponded the phenyl proton at the position *para* to the amino group ($\delta \approx 6.6$ ppm), as well as by the appearance of a signal for the triazole proton (singlet at $\delta \approx 7.15$ ppm), as shown in the Supporting Information, Figure S9. In the ^{1}H NMR spectrum of **G1–4N$_3$-S** (see the Supporting Information, Figure S16), the original peak for the four chloromethyl groups in **G1–4Cl-S** ($\delta = 3.72$ ppm) disappeared, whilst the signal at $\delta = 3.60$ ppm became enhanced, thus indicating that the reaction of **G1–4Cl-S** with sodium azide led to the quantitative formation of the desired azidomethyl group and that the structures of **G2–8Cl-NS** and **G2–8N$_3$-NS** would be confirmed by the occurrence of a similar phenomenon in their ^{1}H NMR spectra. The Supporting Information, Figures S24 and S25 show the ^{1}H NMR spectra of **G4-NS** and **G5-NS** and their chemical shifts were consistent with their structures (Scheme 2), with no unexpected peaks appearing. To further confirm the structures of **G4-NS** and **G5-NS**, their ^{1}H,^{1}H-COSY and ^{1}H,^{13}C-COSY spectra (see the Supporting Information, Figures S26 and S27) were also recorded, which were also consistent with their structures (Scheme 2).

Analysis of the dendritic growth by MS (MALDI-TOF) and by gel-permeation chromatography (GPC; see the Supporting Information, Table S1) was performed for the products after each step, as shown in Scheme 1, Scheme 3, and Scheme 4. MS (MALDI-TOF) was a good method for confirming the exact molecular weight of the dendrimers. The Supporting Information, Figures S28–S35 show the mass spectra of the prepared dendrimers (Scheme 1, Scheme 3, and Scheme 4) and all of the experimental results were in good agreement with their expected molecular weights from their structures. Compared to the other dendrimers, **G1–4N$_3$-S** and **G2–8N$_3$-NS** did not give neat signals, which should have been caused by the fragment ions owing to fragmentation of the unstabilized azide groups during MS analysis. Unfortunately, we failed to detect any signals



Scheme 5. Synthesis of the **G2-4N$_3$-NS** dendrimer core.

Table 1. Synthesis of dendrimers **G4-NS** and **G5-NS**.

	G0-≡-N	G1-≡-NS	G2-≡-NS
Compound **1**	**G1-N**	**G2-NS**	**G3-NS**
G1-4N$_3$-N	–	**G3-NS**[a]	–
G1-4N$_3$-S	**G2-NS**	–	**G4-NS**[a]
G2-8N$_3$-NS	**G3-NS**	–	**G5-NS**[a]

[a] These routes were chosen in this work.

within the appropriate mass range for **G4-NS** and **G5-NS**, possibly because their larger molecular weight resulted in much-lower peak intensity. All of the GPC curves of the dendrimers showed narrow peaks, thus indicating that the products possessed monodisperse molecular weights. However, in general, the characterization by GPC was of limited value because the dendrimers themselves were less polydisperse than the polystyrene standards that were used for the calibration; despite this drawback, the GPC results could still confirm the success of the reaction to some degree.

The dendrimers were thermally stable, as shown in the Supporting Information, Figure S36, and the 5%-weight-loss temperatures of the polymers are listed in Table 2. The degradation temperatures (T_d) for the dendrimers were above 200 °C, thus revealing that they were thermally stable. Upon increasing the generation number, T_d decreased, possibly owing to increasing loading density of the effective chromophore moieties in the dendrimers. The glass-transition temperatures (T_g) of the dendrimers were also investigated by using differential scanning calorimetry (DSC, Table 2).

G2-NS and **G3-NS** were soluble in common polar organic solvents, such as $CHCl_3$, THF, DMF, and DMSO. The solubility of **G4-NS** and **G5-NS** was a littler poorer than that of **G2-NS** and **G$_3$-NS**, owing to their high molecular weight; however, they were still soluble in DMF and DMSO. As demonstrated in their UV/Vis spectra, **G4-NS** and **G5-NS** exhibited good site-isolation effects in comparison with the free chromophore molecules and low-generation dendrimers **G2-NS** and **G3-NS**, thereby revealing that the exterior benzene moieties and the interior triazole rings that surrounded the azo chromophore moieties played a key role in shielding these moieties from the solvatochromic effect (see the Supporting Information, Figures S37–S42 and Table S2). The enhanced effective-site isolation that was achieved in **G4-NS** and **G5-NS** would directly impede the strong intermolecular dipole–dipole interactions between the chromophore moieties and be highly beneficial to the

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Table 2. Physical and NLO data of the dendrimers.

	T_g[a] [°C]	T_d[b] [°C]	T_e[c] [°C]	d_{33}[d] [pm V^{-1}]	$d_{33(\infty)}$[e] [pm V^{-1}]	Φ[f]	N[g]
G2-NS	81	282	105	113.8	20.1	0.21	0.517
G3-NS	93	236	95	165.0	29.2	0.28	0.547
G4-NS	107	219	135	175.3	35.8	0.31	0.565
G5-NS	99	206	125	253.0	51.7	0.40	0.571

[a] Temperature that caused 5% weight-loss in the polymers, determined by TGA analysis under a nitrogen atmosphere at a heating rate of 10°C min^{-1}. [b] Glass-transition temperature (T_g) of the polymers, determined by DSC analysis under an argon atmosphere at a heating rate of 10°C min^{-1}. [c] The best poling temperature. [d] Second harmonic generation (SHG) coefficient. [e] Nonresonant d_{33} values, which were calculated by using the approximate two-level model. [f] Order parameter $\Phi = 1\,A_1A_0^{-1}$, where A_1 and A_0 are the absorbance of the polymer film after and before corona poling, respectively. [g] Loading density of the effective chromophore moieties, which was calculated as the total molecular weight of all of the chromophores (main chromophore and isolation chromophore) divided by the molecular weight of the dendrimers.

ordered noncentrosymmetric alignment of the chromophore moieties during the poling process. In addition, owing to the presence of sulfonyl chromophores, all of the maximum absorptions of the dendrimers that contained the isolation chromophore were blue-shifted compared with that containing only one type of chromophore; these blue-shifted maximum absorptions of the dendrimers would result in a wide optical-transparency window and contribute to practical applications in the field of photonics.

NLO properties: A convenient technique to study the second-order NLO activity was to investigate the second-harmonic-generation (SHG) processes that were characterized by their d_{33} value, which was an SHG coefficient. The test procedure was similar to that reported previously[12] 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** (100.0 pm V^{-1}) to **G5** (193.1 pm V^{-1}), with an accompanying increase in the loading density of the chromophore moieties and the more-perfect 3D structure of the dendrimers.[10] Herein, a similar phenomenon was observed: changing the loading concentration of the chromophore moieties from 0.517 in **G2-NS** (because the sulfonyl-based azo chromophores could also directly contribute to the macroscopic NLO effect, the loading concentration of the chromophore moieties also contain isolation chromophores in this paper) to 0.547 in **G3-NS**, 0.565 in **G4-NS**, and 0.571 in **G5-NS** led to an increase in the NLO coefficients from 113.8 (**G2-NS**) to 165.0 (**G3-NS**), 175.3 pm V^{-1} (**G4-NS**), and 253.0 pm V^{-1} (**G5-NS**). These encouraging results should be ascribed to their more-perfect 3D structure and to the isolation effect of the exterior benzene moieties and the interior triazole rings, which could impede the interactions and enhance the poling efficiency, according to the concept of the “suitable isolation group”.

In comparison with **G5**, which only contained one kind of chromophore (the nitro-based chromophore), **G5-NS** demonstrated much-higher NLO coefficients (**G5-NS**: d_{33} = 253.0 pm V^{-1}, **G5**: d_{33} = 193.1 pm V^{-1}). This result should be ascribed to the presence of the isolation (sulfonyl-based) chromophore, similar to the case of **P1**–**P4**. This result could be explained by the fact that the $\mu\beta$ value of the sulfonyl-based chromophore was lower than that of the nitro-based one; thus, the sulfonyl-based moieties and the triazole groups acted as isolation groups to facilitate the noncentrosymmetric alignment of the nitro-based chromophore moieties in the dendrimers in the electronic field to contribute to the macroscopic NLO effect. On the other hand, the sulfonyl-based chromophore groups themselves could be well-isolated by the triazole moieties, which should be large enough to shield the electronic interactions between the chromophore moieties owing to their relatively low $\mu\beta$ value, to contribute to the macroscopic NLO effect. From **G2-NS** to **G5-NS**, the 3D structure of the alternating nitro- and sulfonyl-based azo-chromophore moieties became more perfect; also, the loading density of the effective chromophore moieties increased continuously, thus leading to the increasing trend of the tested macroscopic NLO effects. This result confirmed that the sulfonyl-based chromophore could act as an isolation group for the nitro chromophore and lead to the enhanced NLO effect on one hand, whilst, on the other hand, the special 3D structure of the dendrimers really benefit the macroscopic NLO effect.

Because there might be some resonant enhancement owing to the absorption of the chromophore moieties at 532 nm, the NLO properties of the dendrimers should be smaller ($d_{33(\infty)}$, Table 2). Owing to their good wide optical transparency, as well as their outstanding large d_{33} values, the $d_{33(\infty)}$ values of the dendrimers were still very high (20.1, 29.2, 35.8, and 51.7 pm V^{-1}); as such, these dendrimers have potential applications in the field of optics. This result means that the introduction of isolation chromophores into the dendrimers (or polymers) is a new way to solve the contradictions between nonlinearity and transparency. However, to obtain more information on these isolation chromophores, further research is still needed.

To further explore the alignment of the chromophore moieties in these dendrimers, we measured their order parameter (Φ). According to the equation given in the footnote in Table 2, the Φ values of the dendrimers were calculated and their results are listed in Table 2 (also see the Supporting Information, Figures S43–S46). The trend in the Φ values was the same as that in the d_{33} values of the dendrimers, which further confirmed our theory.

Depoling experiments of the dendrimers were conducted in which the real-time decays of their SHG signals were monitored as the poled films were heated from 35 to 130°C in air at a rate of 4°C min^{-1}. The Supporting Information, Figure S47, shows the decay of the SHG coefficient of the dendrimers as a function of temperature. For **G2-NS** and **G3-NS**, the temperatures for decay were only 70°C, whilst those of **G4-NS** and **G5-NS** increased to 92 and 82°C, respectively, which should be attributed to the 3D macromolecular architecture that might suppress the relaxation of the ordered dipole alignment to some degree. Thus, coupled with their large NLO effects and improved optical transparency, **G5-NS** might be a promising candidate for practical NLO applications.

Conclusion

In summary, by using a combination of divergent and convergent approaches with the powerful click-chemistry reaction, high-generation dendrimers **G3-NS**, **G4-NS**, and **G5-NS** were successfully obtained; this synthesis confirmed the advantage of the "double-stage" method for the preparation of dendrimers. The high d_{33} values of these dendrimers, in particular, the trend of increasing d_{33} value with increasing the loading concentration of the chromophore moieties, realized our idea of the chromophore as an isolation group for another NLO chromophore with a higher $\mu\beta$ value and further confirmed that the frequently observed asymptotic dependence of electro-optic activity on chromophore density may be overcome through rational design. Thus, these successful examples may open up a new avenue for the synthesis of more NLO dendrimers and this synthetic strategy will aid other scientists in the preparation of high-generation dendrimers.

Experimental Section

Materials and instrumentation: THF was dried over and distilled from a K–Na alloy under an atmosphere of dry nitrogen. Triethylamine was distilled at atmospheric pressure and kept over potassium hydroxide. CH_2Cl_2 was dried over and distilled from CaH_2 at atmospheric pressure before use. DMF was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. *N*,*N*-Di(4-pentynyl)benzenamine (**S1**), 4-ethylsulfonylbenzenediazonium fluoroborate (**S2**), 4-nitrobenzenediazonium fluoroborate (**S3**), chromophore **S4**, and compounds **1**, **3**, **5**, **G1-N**, and **G1–4N_3-N** were prepared according to our previously reported procedures.[9a,10,13] Compounds **2** and **4** were synthesized according to our previous work.[9a,13] *N*,*N*,*N*,*N*,*N*-pentamethyldiethylenetriamine (PMDETA) was purchased from Alfa Aesar. All other reagents were used as received.

^{1}H and ^{13}C NMR spectra were measured on a Varian Mercury300 spectrometer by using tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard; ^{13}C NMR, ^{1}H,^{1}H-COSY, and ^{1}H,^{13}C-COSY spectra of **G4-NS** and **G5-NS** were measured on a Bruker ARX 400 spectrometer. FTIR spectra were recorded on a PerkinElmer-2 spectrometer in the region 3000–400 cm^{-1}. UV/Vis spectra were obtained on a Shimadzu UV-2550 spectrometer. MS (MALDI-TOF) were measured on a Voyager-DE-STR MALDI-TOF mass spectrometer (ABI, American) that was equipped with a 337 nm nitrogen laser and a 1.2 m linear flight path in positive-ion mode. Elemental analysis was performed on a CARLOERBA-1106 microelemental analyzer. Gel-permeation chromatography (GPC) was used to determine the molecular weight of the polymers. GPC analysis was performed on a Waters HPLC system that was equipped with a 2690D separation module and a 2410 refractive-index detector. Polystyrene standards were used as the calibration standards in the GPC analysis. THF was used as an eluent and the flow rate was 1.0 mL min^{-1}. Thermal analysis was performed on a NETZSCH STA449C thermal analyzer at a heating rate of 10 °C min^{-1} under a flow of nitrogen (flow rate: 50 cm^3 min^{-1}) for thermogravimetric analysis (TGA). The thermal transitions of the polymers were investigated on a METTLER DSC822e differential scanning calorimeter under a nitrogen atmosphere at a scanning rate of 10 °C min^{-1}. The thermometer for measurement of the melting point was uncorrected. The thickness of the films was measured on an Ambios Technology XP-2 profilometer.

Synthesis of dendrimer G1-≡-NS: Diazonium salt **2** (224.2 mg, 0.675 mmol) and dendrimer **G1** (662.7 mg, 0.450 mmol) were dissolved in DMF/THF (6 mL/3 mL) at 0 °C. The mixture was stirred for 40 h at 0 °C and was subsequently treated with H_2O, extracted with $CHCl_3$, and washed with brine. The organic layer was dried over anhydrous sodium sulfate. After removal of the organic solvent, the crude product was purified by column chromatography on silica gel (EtOAc) to afford **G_1-≡-NS** as a red solid (684.4 mg, 89.1 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): $\delta = 1.96$ (m, 2H; CH_2C), 2.05 (s, 1H; C≡CH), 2.24 (m, 4H; CH_2), 2.62 (m, 2H; CH_2), 2.96 (t, $J = 7.5$ Hz, 4H; CH_2C), 3.26 (t, $J = 5.7$ Hz, 2H; SCH_2), 3.71 (br s, 4H; NCH_2), 3.94 (br s, 8H; NCH_2), 4.14 (t, $J = 6.0$ Hz, 4H; NCH_2), 4.37 (br s, 4H; OCH_2), 4.59 (t, $J = 6.0$ Hz, 8H; $COOCH_2$), 6.56 (d, $J = 8.4$ Hz, 2H; ArH), 6.96 (d, $J = 9.0$ Hz, 4H; ArH), 7.23 (s, 2H; C=CH), 7.42 (t, $J = 7.5$ Hz, 8H; ArH), 7.53–7.65 (m, 7H; ArH), 7.75–7.91 (m, 12H; ArH), 7.98 ppm (d, $J = 7.5$ Hz, 8H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): $\delta = 17.13$, 21.68, 28.27, 47.05, 49.70, 51.2, 54.88, 61.58, 68.31, 70.21, 108.97, 111.76, 116.34, 117.29, 122.26, 122.88, 126.09, 128.38, 128.94, 129.47, 133.22, 144.76, 146.66, 147.02, 148.08, 149.20, 150.68, 154.93, 155.68, 166.33; IR (KBr): $\tilde{\nu} = 3289$ (C≡CH), 1716 (C=O), 1514, 1338 (NO_2), 1140 ppm (SO_2); MS (MALDI-TOF): *m*/*z* calcd for $C_{91}H_{87}N_{17}O_{16}S$: 1728.6 $[M+Na]^+$; found: 1728.8; elemental analysis calcd (%) for $C_{91}H_{87}N_{17}O_{16}S$: C 64.04, H 5.14, N 13.95; found: C 63.64, H 5.31, N 13.70.

Synthesis of dendrimer G2-NS: Chromophore **G1-≡-NS** (510.0 mg, 0.299 mmol), *N*,*N*-bis(2-azidoethyl)aniline (**2**, 31.4 mg, 0.136 mmol), $CuSO_4 \cdot 5H_2O$ (10 mol %), $NaHCO_3$ (20 mol %), and ascorbic acid (20 mol %) were dissolved in THF/water (5 mL/1 mL) under a nitrogen atmosphere in a Schlenk flask. The mixture was stirred at RT for 8 h, extracted with $CHCl_3$, and washed with brine. The organic layer was dried over anhydrous magnesium sulfate and purified by column chromatography on silica gel (THF/$CHCl_3$, 1:1) to afford **G2-NS** as a red solid (339 mg, 77.6 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): $\delta = 1.81$ (br s, CH_2), 2.05 (br s, CH_2), 2.23 (br s, CH_2C), 2.78 (br s, CH_2C), 2.94 (br s, CH_2C), 3.13 (br s, SCH_2), 3.62 (br s, NCH_2), 3.71 (br s, NCH_2), 3.93 (br s, NCH_2), 4.13 (br s, NCH_2), 4.36 (br s, OCH_2), 4.56 (br s, $COOCH_2$), 6.58 (d, $J = 8.4$ Hz; ArH), 6.79 (br s, ArH), 7.05 (m; ArH), 7.15 (br s, ArH), 7.43 (m; ArH), 7.52–7.63 (m; ArH), 7.76–8.00 ppm (m; ArH and C=CH); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): $\delta = 22.18$, 23.00, 24.16, 24.30, 28.77, 29.53, 47.62, 47.78, 50.26, 51.50, 51.99, 55.60, 62.10, 68.03, 68.88, 108.31, 109.54, 112.08, 112.30, 113.34, 116.91, 117.85, 119.07, 122.86, 123.36, 126.41, 126.63, 128.91, 129.44, 129.99, 130.31, 133.72, 139.22, 144.93, 145.28, 146.34, 147.20, 147.50, 148.61, 149.68, 151.23, 155.44, 156.11, 166.87 ppm; IR (KBr): $\tilde{\nu} = 1716$ (C=O), 1514, 1338 (NO_2), 1139 (SO_2); MS (MALDI-TOF): *m*/*z* calcd for $C_{192}H_{187}N_{41}O_{32}S_2$: 3669.2 $[M+Na]^+$; found: 3667.9; elemental analysis calcd (%) for $C_{192}H_{187}N_{41}O_{32}S_2$: C 63.27, H 5.17, N 15.76; found: C 62.39, H 5.23, N 15.75.

Synthesis of dendrimer G2-≡-NS: The procedure was similar to that of dendrimer **G1-≡-NS** by using dendrimer **G2-NS** (250 mg, 0.0686 mmol) and diazonium salt **3** (65.6 mg, 0.206 mmol). The crude product was purified by column chromatography on silica gel (THF/$CHCl_3$, 2:1) to afford **G2-≡-NS** as a red solid (190.1 mg, 71.5 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): $\delta = 1.84$ (br s, CH_2), 1.95–2.10 (br s, CH_2 and C≡CH), 2.22 (br s, CH_2), 2.48 (br s, CH_2C), 2.81 (br s, CH_2C), 2.94 (br s, CH_2C), 3.13 (br s, SCH_2), 3.71 (br s, NCH_2), 3.93 (br s, NCH_2), 4.13 (br s, NCH_2), 4.20–4.50 (br s, OCH_2), 4.56 (br s, $COOCH_2$), 6.54 (d, $J = 8.4$ Hz; ArH), 6.70 (d, $J = 8.4$ Hz; ArH), 6.95 (d, $J = 8.4$ Hz; ArH), 7.41 (m; ArH), 7.52–7.63 (m; ArH), 7.76–8.00 ppm (m; ArH and C=CH); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): $\delta = 21.68$, 23.82, 28.30, 29.04, 47.10, 49.76, 50.97, 55.02, 61.63, 67.52, 68.39, 107.80, 109.04, 111.78, 116.38, 117.33, 112.36, 122.88, 126.11, 128.39, 128.91, 129.49, 133.22, 144.77, 147.06, 148.10, 150.73, 154.91, 166.38 ppm; IR (KBr): $\tilde{\nu} = 3289$ (C≡CH), 1717 (C=O), 1515, 1339 (NO_2), 1142 (SO_2); MS (MALDI-TOF): *m*/*z* calcd for ($C_{203}H_{196}N_{44}O_{35}S_2$): *m*/*z* $[M+Na]^+$: 3899.1; found: *m*/*z* 3900.9; elemental analysis calcd (%) for $C_{203}H_{196}N_{44}O_{35}S_2$: C 62.90, H 5.10, N 15.90; found: C 62.01, H 5.10, N 15.33.

Synthesis of dendrimer G2–4Cl-S: The procedure was similar to that of dendrimer **G2-NS** by using compound **4** (497.6 mg, 1.10 mmol) and *N*,*N*-bis(2-azidoethyl)aniline (**1**, 115.6 mg, 0.50 mmol). The crude product was purified by column chromatography on silica gel (EtOAc) to afford **G1–4Cl-S** as an orange solid (514.1 mg, 90.5 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): $\delta=2.08$ (m, 4H; CH_2), 2.81 (brs, 4H; CH_2C), 3.16 (brs, 4H; SCH_2), 3.64 (brs, 4H; NCH_2), 3.72 (brs, 8H; CH_2Cl), 3.86 (brs, 8H; NCH_2), 4.35 (brs, 4H; NCH_2), 6.63 (d, $J=7.2$ Hz, 2H; ArH), 6.79 (d, $J=7.2$ Hz, 5H; ArH), 7.15 (s, 2H; C=CH), 7.80–8.00 ppm (m, 14H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): $\delta=22.52$, 23.67, 40.11, 47.24, 51.49, 53.28, 55.13, 111.52, 112.79, 118.49, 122.21, 122.85, 125.97, 128.97, 129.81, 138.59, 144.31, 145.87, 149.45, 155.90 ppm; IR (KBr): $\tilde{\nu}=1131$ (SO_2); MS (MALDI-TOF): *m*/*z* calcd for ($C_{52}H_{59}N_{13}O_4S_2Cl_4$): *m*/*z* $[M+Na]^+$: 1159.0; found: *m*/*z* 1158.5; elemental analysis calcd (%) for $C_{52}H_{59}N_{13}O_4S_2Cl_4$: C 54.98, H 5.23, N 16.03; found: C 54.95, H 5.10, N 15.50.

Synthesis of dendrimer G1–4N$_3$-S: A Schlenk flask was charged with compound **G1–4Cl-S** (284 mg, 0.25 mmol), NaN_3 (130 mg, 2.0 mmol), and DMF (2.5 mL). The mixture was stirred at 80 °C for 12 h and the solution was poured into a large volume of water. The precipitate was collected and washed several times with water and MeOH/water (1:1) and then dried under vacuum to afford the product as an orange solid (275 mg, 94.6 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): $\delta=2.07$ (m, 4H; CH_2), 2.80 (brs, 4H; CH_2C), 3.16 (t, $J=7.8$ Hz, 4H; SCH_2), 3.60 (brs, 8H; CH_2N_3), 3.69 (brs, 4H; NCH_2), 4.35 (brs, 4H; NCH_2), 6.62 (d, $J=8.1$ Hz, 2H; ArH), 6.81 (d, $J=8.1$ Hz, 5H; ArH), 7.16 (s, 2H; C=CH), 7.80–8.00 ppm (m, 14H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): $\delta=22.26$, 23.41, 46.91, 48.26, 50.15, 51.00, 54.82, 111.44, 112.30, 117.89, 121.95, 122.50, 125.62, 128.65, 129.39, 138.18, 143.80, 145.30, 145.51, 149.59, 155.60 ppm; IR (KBr): $\tilde{\nu}=2097$ (N_3), 1131 (SO_2); MS (MALDI-TOF): *m*/*z* calcd for $C_{52}H_{59}N_{25}O_4S_2$: 1184.5 $[M+Na]^+$; found: 1184.7; elemental analysis calcd (%) for $C_{52}H_{59}N_{25}O_4S_2$: C 53.73, H 5.12, N 30.13; found: C 53.42, H 5.26, N 30.02.

Synthesis of dendrimer G2–8Cl-NS: The procedure was similar to that of dendrimer **G2-NS** by using compound **4** (241 mg, 0.533 mmol) and **G1–4N$_3$-N** (140 mg, 0.121 mmol). The crude product was purified by column chromatography on silica gel (THF/$CHCl_3$, 1:1) to afford **G2–8Cl-NS** as a red solid (293 mg, 81.5 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): $\delta=1.80$–2.30 (CH_2), 2.80 (brs, CH_2C), 2.91 (brs, CH_2C), 3.14 (brs, SCH_2), 3.71 (brs, NCH_2), 3.85 (brs, CH_2Cl), 3.94 (brs, NCH_2), 4.14 (brs, NCH_2), 4.32 (brs, NCH_2), 4.40 (brs, NCH_2), 6.56 (brs, ArH), 6.76 (brs, ArH), 7.15–7.33 (ArH and C=CH), 7.60 (brs, ArH), 7.70–8.00 ppm (ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): $\delta=21.74$, 22.47, 23.64, 23.80, 27.67, 28.52, 29.07, 40.15, 47.10, 51.13, 53.22, 55.06, 67.48, 68.44, 107.77, 109.15, 111.55, 111.81, 112.76, 116.25, 117.26, 122.23, 122.49, 122.83, 125.94, 128.91, 129.62, 138.56, 144.26, 145.16, 146.09, 146.33, 146.80, 148.31, 149.13, 149.58, 155.18, 155.83 ppm; IR (KBr): $\tilde{\nu}=1511$, 1343 (NO_2), 1131 (SO_2); MS (MALDI-TOF): *m*/*z* calcd for $C_{136}H_{149}N_{39}O_{14}S_4Cl_8$: 2988.8 $[M+Na]^+$; found: 2989.5; elemental analysis calcd (%) for $C_{136}H_{149}N_{39}O_{14}S_4Cl_8$: C 55.08, H 5.06, N 18.42; found: C 55.35, H 5.30, N 17.47.

Synthesis of dendrimer G2–8N$_3$-NS: The procedure was similar to that of dendrimer **G1–4N$_3$-S** by using **G2–8Cl-NS** (80 mg, 0.027 mmol) and NaN_3 (28.1 mg, 0.43 mmol). The reaction was stirred at 80 °C for 12 h and the solution was poured into a large volume of water. The crude product was purified by repeated precipitation of its solution in THF with MeOH to afford **G2–8N$_3$-NS** as a red solid (71.9 mg, 88.4 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): $\delta=1.80$–2.30 (CH_2), 2.80 (brs, CH_2C), 2.91 (brs, CH_2C), 3.14 (brs, SCH_2), 3.59 (brs, CH_2N_3), 3.71 (brs, NCH_2), 3.95 (brs, NCH_2), 4.15 (brs, NCH_2), 4.33 (brs, NCH_2), 4.43 (brs, NCH_2), 6.56 (brs, ArH), 6.76 (brs, ArH), 7.15–7.33 (ArH and C=CH), 7.60 (brs, ArH), 7.70–8.00 ppm (ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): $\delta=21.60$, 22.77, 46.26, 47.79, 49.75, 54.20, 110.90, 121.49, 121.93, 125.04, 128.03, 145.24, 148.89, 155.06 ppm; IR (KBr): $\tilde{\nu}=2096$ (N_3), 1511, 1341 (NO_2), 1130 (SO_2); MS (MALDI-TOF): *m*/*z* calcd for $C_{136}H_{149}N_{63}O_{14}S_4$: 3039 $[M+Na]^+$; found: 3038; elemental analysis calcd (%) for $C_{136}H_{149}N_{63}O_{14}S_4$: C 54.12, H 4.95, N 29.24; found: C 54.07, H 5.30, N 28.85.

Synthesis of dendrimer G3-NS: The procedure was similar to that of **G1-NS** by using chromophore **G1-≡-NS** (150.2 mg, 0.088 mmol) and **G1–4N$_3$-N** (23.1 mg, 0.020 mmol). The crude product was purified by column chromatography on silica gel (THF) to afford **G3-NS** as a red solid (134 mg, 84.0 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): $\delta=1.85$ (brs, CH_2), 2.05 (brs, CH_2), 2.21 (brs, CH_2C), 2.77 (brs, CH_2C), 2.92 (brs, CH_2C), 3.11 (brs, SCH_2), 3.69 (brs, NCH_2), 3.92 (brs, NCH_2), 4.12 (brs, NCH_2), 4.36 (brs, OCH_2), 4.54 (brs, $COOCH_2$), 6.53 (d, $J=8.4$ Hz; ArH), 6.66 (brs, ArH), 6.95 (m; ArH), 7.15 (brs, ArH), 7.52–7.63 (m; ArH), 7.76–8.00 ppm (m; ArH and C=CH); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): $\delta=21.68$, 23.61, 28.29, 30.17, 47.01, 49.73, 51.00, 61.60, 68.39, 109.01, 111.75, 116.35, 117.27, 122.36, 122.82, 125.39, 126.08, 128.37, 129.46, 133.19, 138.62, 144.75, 146.65, 147.00, 148.04, 150.70, 154.94, 166.33 ppm; IR (KBr): $\tilde{\nu}=1717$ (C=O), 1514, 1338 (NO_2), 1141 (SO_2); MS (MALDI-TOF): *m*/*z* calcd for $C_{416}H_{405}N_{95}O_{70}S_4$: 8007 $[M+Na]^+$; found: 8010; elemental analysis calcd (%) for $C_{416}H_{405}N_{95}O_{70}S_4$: C 62.58, H 5.11, N 16.67; found: C 62.91, H 5.47, N 16.16.

General procedure of the synthesis of G4-NS and G5-NS: A mixture of **G1–4N$_3$-N** or **G2–8N$_3$-NS** (1.00 equiv), **G2-≡-NS** (4.4 equiv or 8.8 equiv), and CuBr (1.00 equiv) was dissolved in DMF (0.02 M **N$_3$**) under a nitrogen atmosphere in a Schlenk flask. *N*,*N*,*N*,*N*,*N*-pentamethyldiethylenetriamine (PMDETA, 1.00 equiv) was added and the mixture was stirred at 25–30 °C for 6 h before being quenched by the addition of water. The product was purified by repeating precipitation of its solution in DMF with acetone. The precipitate was filtered, washed with THF, and dried under vacuum at 40 °C to a constant weight.

G4-NS: **G1–4N$_3$-N** (5.8 mg, 0.0050 mmol) and **G2-≡-NS** (85.3 mg, 0.022 mmol). **G4-NS** was obtained as red powder (60.0 mg, 72.0 %). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 298 K): $\delta=1.7$–2.2 (CH_2), 2.7–2.9 (CH_2C), 3.6–3.8 (NCH_2), 3.8–4.0 (NCH_2), 4.1–4.2 (NCH_2), 4.2–4.6 (CH_2O and CH_2OCO), 6.6–6.9 (ArH), 6.9–7.2 (ArH), 7.3–8.0 ppm (ArH); IR (KBr): $\tilde{\nu}=1717$ (C=O), 1515, 1339 (NO_2), 1138 (SO_2); elemental analysis calcd (%) for $C_{864}H_{843}N_{201}O_{144}S_{10}$: C 62.26, H 5.10, N 16.89; found: C 62.09, H 4.86, N 15.94.

G5-NS: **G2–8N$_3$-NS** (7.6 mg, 0.0025 mmol) and **G2-≡-NS** (85.3 mg, 0.022 mmol). **G5-NS** was obtained as a red powder (66.0 mg, 77.6 %). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 298 K): $\delta=1.7$–2.2 (CH_2), 2.7–2.9 (CH_2C), 3.6–3.8 (NCH_2), 3.8–4.0 (NCH_2), 4.1–4.2 (NCH_2), 4.2–4.6 (CH_2O and CH_2OCO), 6.6–6.9 (ArH), 6.9–7.2 (ArH), 7.3–8.0 ppm (ArH); IR (KBr): $\tilde{\nu}=1716$ (C=O), 1514, 1338 (NO_2), 1132 (SO_2); elemental analysis calcd (%) for $C_{1760}H_{1717}N_{415}O_{294}S_{20}$: C 62.12, H 5.09, N 17.08; found: C 61.83, H 4.92, N 16.14.

Preparation of polymer thin films: Polymers **P1**–**P4** were dissolved in THF (about 3 wt. %), dendrimers **G2-NS** and **G3-NS** were dissolved in THF (about 4 wt. %), and **G5-NS** was dissolved in DMF (about 10 wt. %); the solutions were filtered through syringe filters and the films were spin-coated onto indium-tin-oxide (ITO)-coated glass substrates, which were cleaned sequentially with DMF, acetone, distilled water, and THF in an ultrasound bath before use. Residual solvent was removed by heating the films in a vacuum oven at 40 °C. Thin films of dendrimer **G4-NS** were prepared by a drop-coating method, owing to its poor solubility and film-forming ability.

NLO measurements of poled films: The second-order optical nonlinearity of the dendrimers was determined by in-situ second-harmonic-generation (SHG) experiments in a closed temperature-controlled oven with optical windows and three needle electrodes. The films were kept at 45° to the incident beam and poled inside the oven; the SHG intensity was monitored simultaneously. Poling conditions were as follows: the temperature was different for each polymer (Table 2); voltage: 7.5 kV at the needle point; gap distance: 0.8 cm. The SHG measurements were carried out with a Nd:YAG laser operating at a repetition rate of 10 Hz and a pulse width of 8 ns at 1064 nm. A Y-cut quartz crystal served as the reference.

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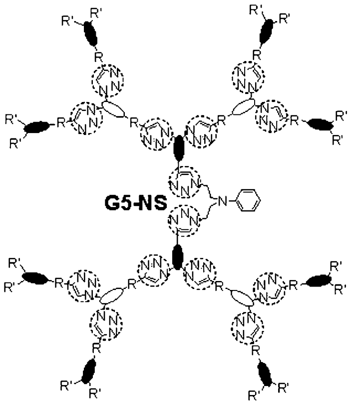
Second's the best: A series of second-order nonlinear optical dendrimers that contained isolation chromophores were conveniently prepared in satisfactory yields through the combination of divergent and convergent approaches coupled with the powerful Sharpless click reaction. Owing to the advantages of the isolation chromophores and the dendrimers, **G5-NS** (see structure) demonstrated large NLO effects and excellent optical transparency.



Dendrimers

W. Wu, C. Li,* G. Yu, Y. Liu, C. Ye, J. Qin, Z. Li* .... ▮▮▮▮–▮▮▮▮

High-Generation Second-Order Nonlinear Optical (NLO) Dendrimers that Contain Isolation Chromophores: Convenient Synthesis by Using Click Chemistry and their Increased NLO Effects

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