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From Nitro- to Sulfonyl-Based Chromophores: Improvement of the Comprehensive Performance of Nonlinear Optical Dendrimers

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Abstract: Through the combination of the divergent and convergent approaches, coupled with the utilization of the powerful Sharpless "click-chemistry" reaction, two series of sulfonyl-based high-generation NLO dendrimers were conveniently prepared with high purity and in satisfactory yields. Thanks to the perfect three-dimensional (3D) spatial isolation from the highly branched structure and the isolation effect of the exterior benzene moieties and the interior triazole rings, these dendrimers exhibited large second harmonic generation coefficient (d_{33}) values up to 181 pm V^{-1}, which, to the best of our knowledge, is the highest value so far for polymers containing sulfonyl-based chromophore moieties. Meanwhile, compared with the nitro-chromophore-based analogues, their optical transparency and NLO stability were improved in a large degree, due to the lower dipole moment (μ) and the special main-chain structure of sulfonyl-based chromophore in these dendrimers.

Keywords: click chemistry · chromophores · dendrimers · nonlinear optics · sulfonyl

Introduction

In the past decades, large efforts have been made to investigate organic and polymeric second-order nonlinear optical (NLO) materials, due to their huge potential applications in photonic devices, such as high-speed electro-optic (EO) modulators, optical switches, and frequency converters.[1] Thanks to the great efforts of scientists, many strategies and approaches have been reported for the development of organic/polymeric NLO materials to meet the basic requirements of practical applications: large optical nonlinearity, low optical loss, and excellent temporal stability of dipole orientation.[2] In particular, controlling the shape of the chromophore has proved to be an efficient approach for minimizing the strong electronic interaction among the high polar chromophore moieties and enhancing the poling efficiency, with a spherical shape, which was proposed by Dalton and Jen et al. as being the most ideal conformation.[2d,3] Applying this site isolation principle, many dendritic NLO materials, including hyperbranched polymers, dendronized polymers, and dendrimers have been prepared and exhibited large EO coefficients, in which some bulky groups were linked to chromophores as the isolation moieties.[4,5] Also, based on these excellent results in the NLO field, as well as our systematic work on the concept of the "suitable isolation group",[6,7] our group have recently prepared a new series of nitro-based chromophore-containing NLO dendrons **G1** to **G5** (Schemes S1–S3, see the Supporting Information) and dendrimers **G1-TPA** to **G3-TPA** (Chart S1 and Schemes S4 and S5, the Supporting Information) through a "double-stage" method by using the "click-chemistry" reaction.[8] These dendrimers demonstrated very large d_{33} values (NLO coefficient, which could express the magnitude of NLO effect) of 193.1 pm V^{-1} (**G5**) and 246.0 pm V^{-1} (**G3-TPA**), and the observed NLO effects increased with an increase of the loading density of the chromophore moieties, indicating that the frequently observed asymptotic dependence of EO activity on the chromophore number density may be overcome through rational design, which is in accordance with the prediction of Sullivan and co-workers.[9] This also confirmed our idea of the formed triazole rings as suitable isolation groups to enhance the macroscopic NLO effect.[10] However, as mentioned above, in addition to the large optical nonlinearity, the optical transparency and the stability of NLO coefficients were also important for NLO materials but less explored by scientists. In fact, there are so-called nonlinearity-transparency trade-offs and nonlinearity-stability trade-offs present in the NLO

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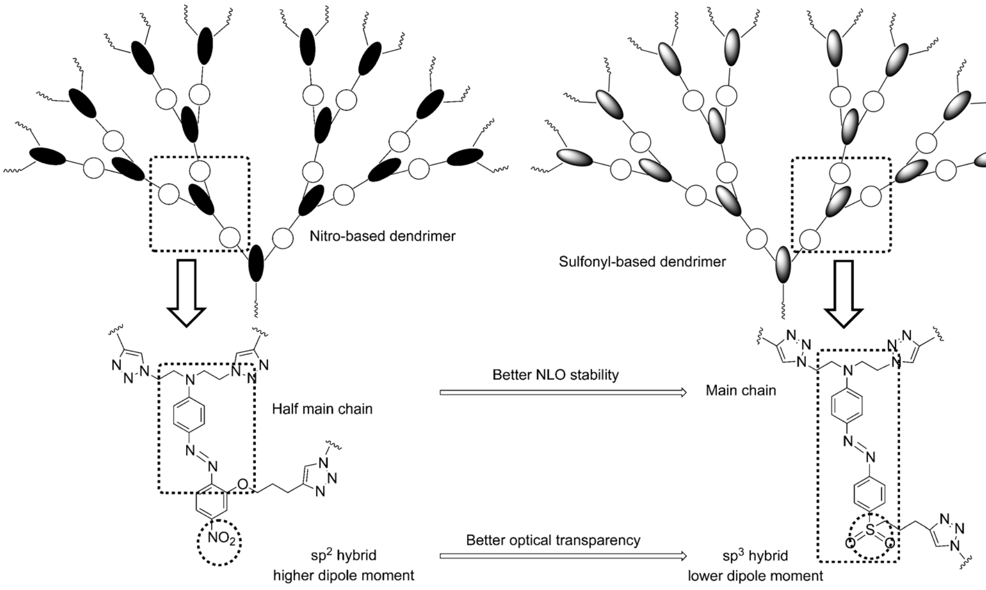


Figure 1. Differences between sulfonyl- and nitro-based-chromophores in NLO dendrimers.

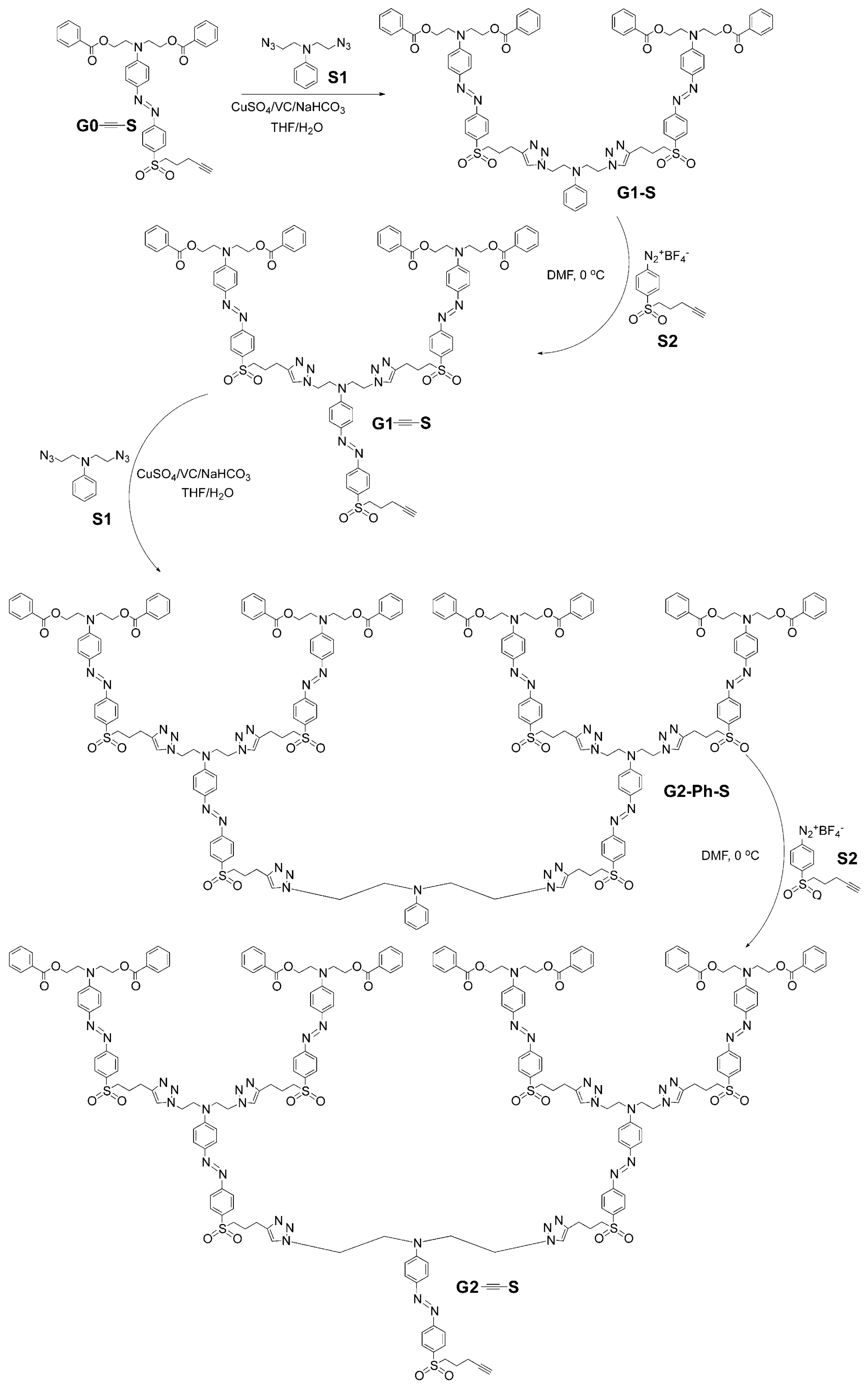
fields,[11] that is to say, the improvement of the NLO properties often accompanies the decreased transparency or NLO stability. Therefore, so far, it is still very difficult to demonstrate all of these properties for NLO materials simultaneously.

On the other hand, similar to the nitro-based azo chromophore, the sulfonyl-based azo chromophore was another normal NLO chromophore, and has a similar chemical structure to its nitro-based counterpart. Considering the successful examples of nitro-chromophore-based NLO dendrimers, we hypothesized about the utilization of the sulfonyl-based chromophore moieties instead of the nitro-based ones. In our opinion, perhaps, there should be at least two advantages (Figure 1). First, in contrast to the nitrogen atom in nitro groups that have sp^2 hybrid orbitals, the molecular orbitals of the sulfur atom in the sulfonyl groups are sp^3 hybrid orbitals, which could lead to a little less conjugation with the donor, and decrease the dipole moment (μ) of the chromophore, thus, improve the transparency of this kind of NLO chromophore.[12] Secondly, different from the nitro-based chromophore in NLO dendrimers **G1** to **G5** or **G1-TPA** to **G3-TPA**, the whole sulfonyl-based chromophore could be bonded into the dendrimers, which could limit the relaxation of the chromophore, and further increase the stability of the alignment of the sulfonyl-based chromophore. Meanwhile, this special main-chain structure could also change the topological structure of NLO dendrimers. However, the effect of this change to the performance of NLO dendrimers is very difficult to predict. Considering all of the differences of these two types of chromophores, it was thus very interesting and important to design and synthesize the sulfonyl-chromophore-based high-generation dendrimers, to check whether this change could improve the optical transparency and the stability of NLO coefficients simultaneously as expected. However, so far, there a no reports concerning this.

Therefore, in this paper, we designed and synthesized a new series of sulfonyl-chromophore-based NLO dendrons **G1-S** to **G5-S** (in which S represents that these dendrons consist of sulfonyl-based chromophores, as to differentiate **G1** to **G5** in our previous work) and a new series of sulfonyl-chromophore-based NLO dendrimers **G1-S-GL** to **G4-S-GL** (in which GL represents that the topological structures of these dendrimers are global-like, as to differentiate **G1-S** to **G5-S**), through a "double-stage" method through the "click-chemistry" reaction. As expected, these dendrimers demonstrated a large NLO effect, good optical transparency, and the improved stability of NLO coefficients simultaneously, thus validating our original idea. More excitingly, the NLO coefficient of **G3-S-GL** was $181\,\mathrm{pm\,V^{-1}}$, which is, to the best of our knowledge, the highest value so far for the polymers containing the sulfonyl-based chromophore moieties. Herein, we present the syntheses, characterization, and properties of these new dendrimers in detail.

Results and Discussion

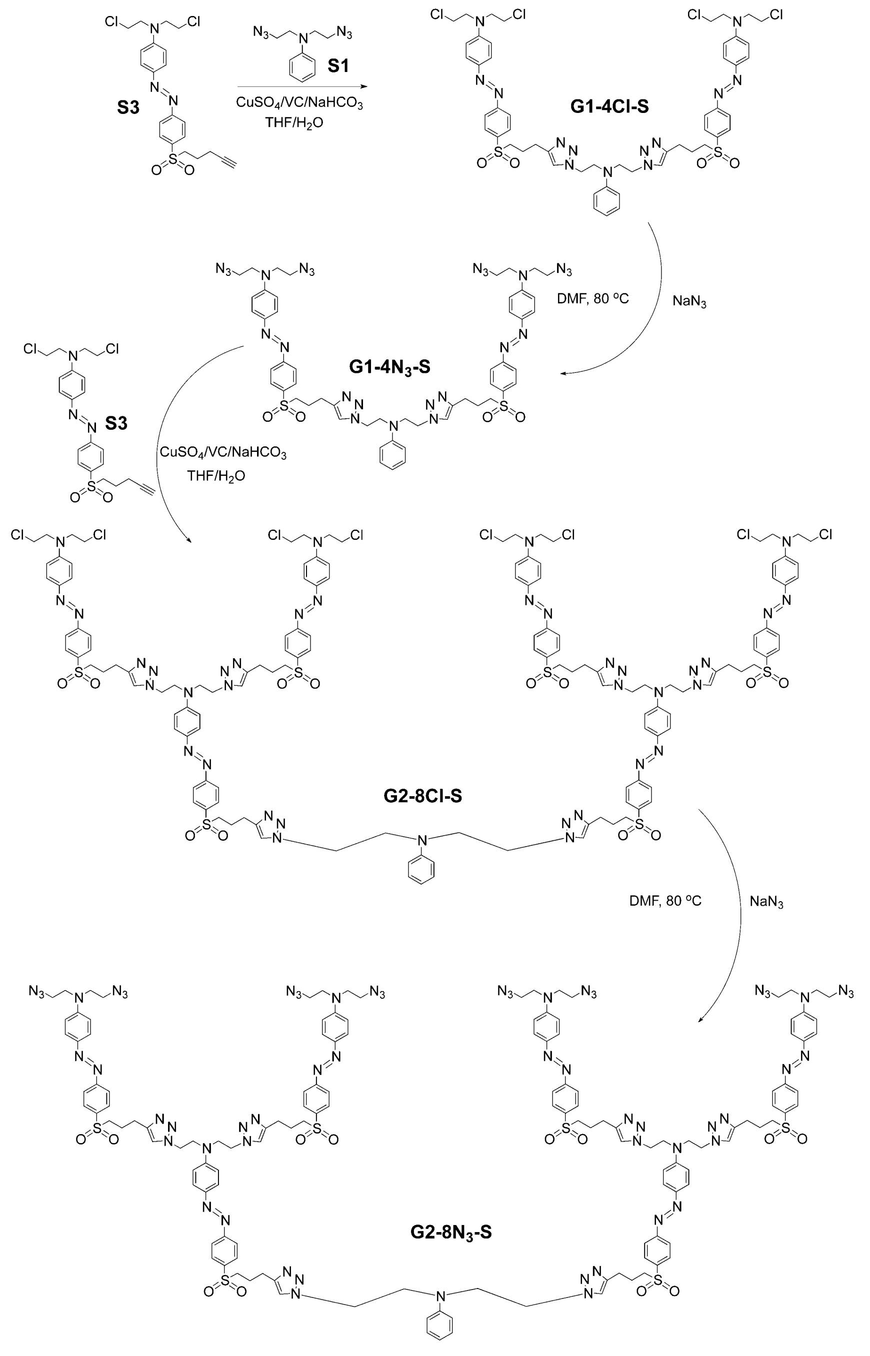
Synthesis: As shown in Schemes 1–3, the synthetic route to **G1-S**–**G5-S** was very similar to our previous syntheses of **G1** to **G5** (Schemes S1–S3, the Supporting Information). In addition, the sulfonyl-based chromophore was used instead of nitro-based one. At first, **G1-S** was synthesized between **G0-≡-S**[6i] and *N,N*-bis(2-azidoethyl)aniline (**S1**),[8] which has been already prepared in our previous work by using "click chemistry" under room temperature. Then, through the efficient azo-coupling reaction at 0 °C, another constructing block of chromophore was formed to yield **G1-≡-S**. Simultaneously, another reactive alkyne group was introduced for



Scheme 1. The synthesis of end-capped dendrons (**G1-≡-S** and **G2-≡-S**). VC = vitamin C

the further growth of the dendrimers. Just repeating these procedures, the low generation dendrons **G1-S** and **G2-S**, and end-capped dendrons **G1-≡-S** and **G2-≡-S** could be easily prepared (Scheme 1). However, the higher generation dendrimers could not be obtained in this convergent approach, because of the large steric hindrance of the reactive segments. Therefore, with the aim to obtain high-generation dendrons, the divergent approach was also used to synthesize the dendronized core **G2-8N$_3$-S** from the AB$_2$-type monomer **G0-2Cl-S**, which was crafted to contain two chloroethyl groups and one terminal alkyne group (Scheme 2). After the "click-chemistry" reaction between **G0-2Cl-S** and *N,N*-bis(2-azidoethyl)aniline (**S1**), the first generation dendron **G1-4Cl-S** was yielded conveniently. Then, through the substitution of the chloride groups in **G1-4Cl-S**, dendron **G1-4N$_3$-S** was produced in high yield. The subsequent click reaction between azides of **G1-4N$_3$-S** and the terminal alkyne in chromophore **G0-2Cl-S** gave the second generation dendrimer of **G2-8Cl**, which could further undergo the substitution reaction of the chloride groups to produce the core **G2-8N$_3$-S** in high yield. At last, the target high-generation dendrons **G3-S** to **G5-S** could be conveniently obtained through "click chemistry" by the utilization of the "double-stage" approach (Scheme 3). Even the preparation of **G5-S**, which has a large steric effect, could proceed completely in about 6 h, as monitored by the FTIR spectra (the peak centered at 2096 cm^{-1} corresponding to the azido groups gradually disappears).

The synthetic route was next improved to give a more efficient preparation of the dendrimers. In our previous case regarding the synthesis of **G1-TPA** to **G3-TPA** (Scheme S4, the Supporting Information),[8c] due to the low reactivity of the Sonogashira coupling reaction used and the difficult purification, the yields of the three-branched core were very low (the total yield of two steps was only 8.99 %). However, in this case, the "click-chemistry" reaction, with nearly quantitative yields and simple product isolation, was used instead

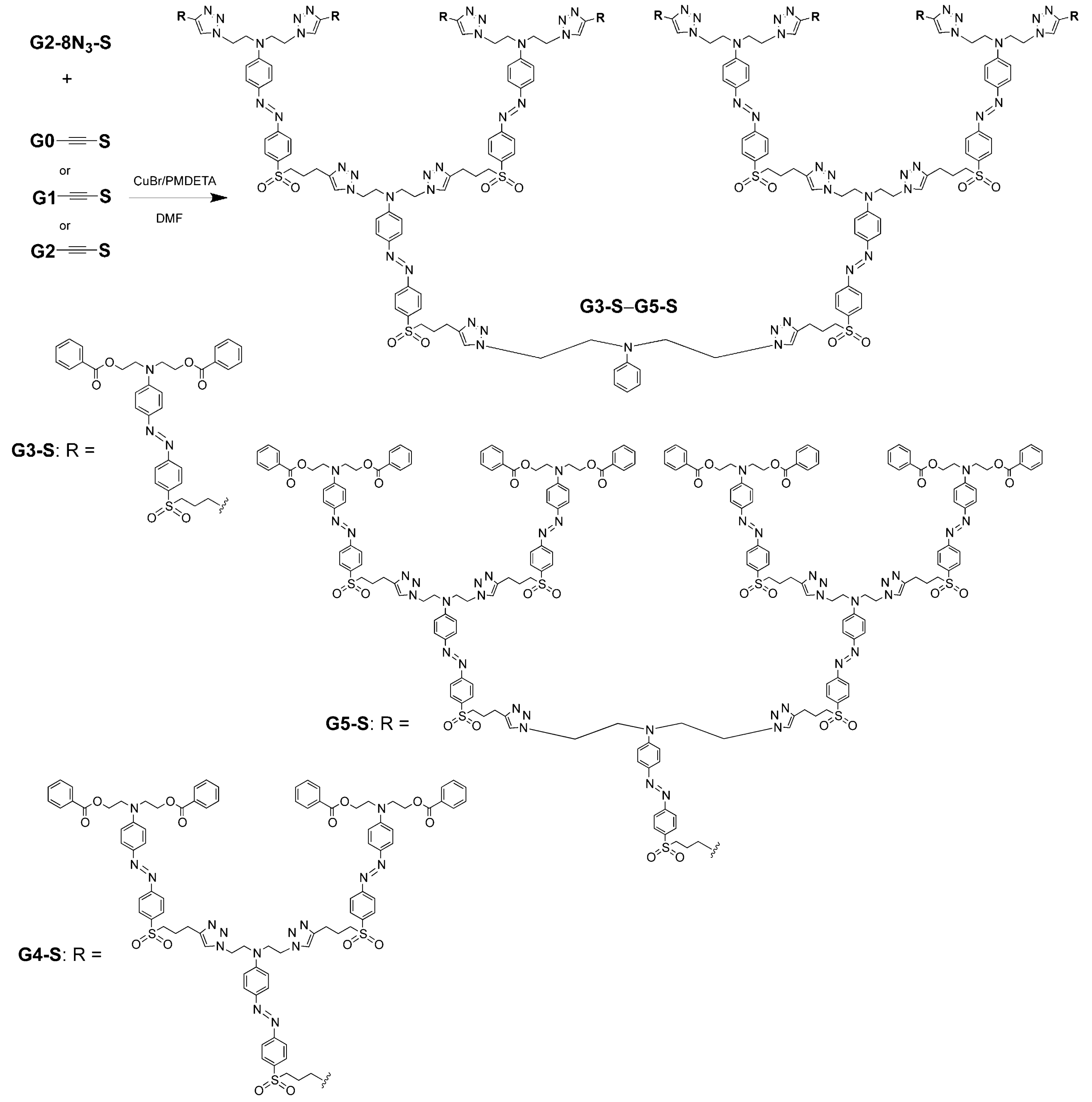


Scheme 2. The synthesis of core **G2-8N$_3$-S**.

(Scheme 4). As expected, in this work the total yield of **G1-6N$_3$-S** through two synthetic steps was up to 67.9%. Meanwhile, to avoid the large isolation effect of the new formed triazoles, the core was changed to phenyl rings (but not the previous TPA units), according to the concept of the "suitable isolation group" (Scheme 4).[6] At last, the target dendrimers **G1-S-GL** to **G4-S-GL** could be conveniently obtained by using the "click chemistry" reaction, by the utilization of the "double-stage" approach. (Scheme 5) These two series of sulfonyl-chromophore-based dendrimers are readily soluble in common polar organic solvents, such as CH_2Cl_2, $CHCl_3$, THF, DMF, and DMSO, and their solutions could be easily spin-coated into thin solid films. Thus, it was convenient to test their NLO and other properties based on the solutions and thin films.

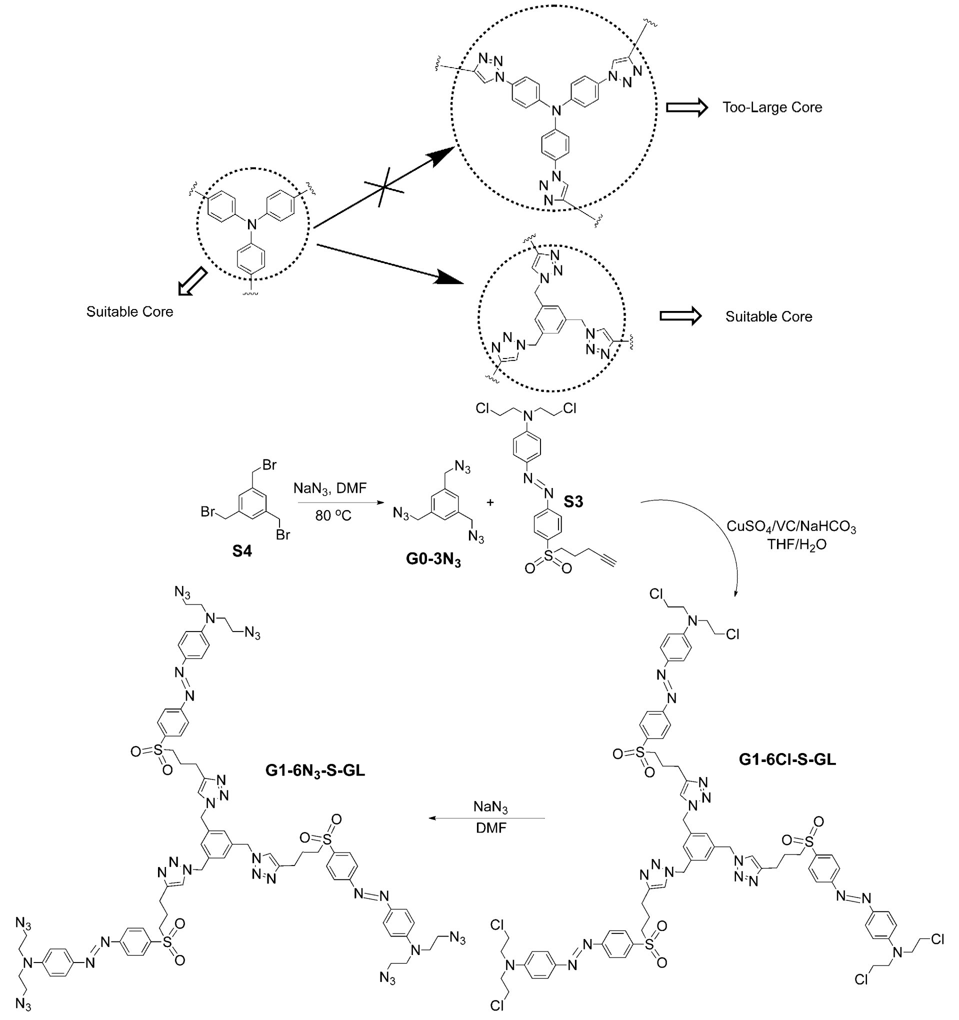
Characterizations: The dendrimers were well characterized by spectroscopic analysis, and all gave satisfactory data, in accordance with their expected molecular structures (see the Experimental Section and the Supporting Information for details). The elemental analysis technology was used to further evaluate the purity of the final target dendrons **G1-S** to **G5-S** and dendrimers **G1-S-GL** to **G4-S-GL**. In the FTIR spectra (Figures S1 and S2, the Supporting Information), all the dendrimers showed absorption bands associated with the sulfonyl groups at about 1316 and 1130 cm^{-1}, indicating the successful introduction of sulfonyl-chromophore moieties into these dendrimers. Meanwhile, the peak of azido groups (at about 2098 cm^{-1}) disappeared in the spectra of the target NLO dendrimers, coupled with the appearance of a carbonyl group absorption at 1717 cm^{-1}, disclosing that the target dendrimers were yielded through the "double-stage" approach successfully.

All the NMR spectra (including ^{1}H and ^{13}C NMR spectra) of these dendrimers are shown in Figure S2–S38 (the Supporting Information). The structures of these dendrimers could be confirmed by the changes of the peaks, associated with the reaction sites, in the ^{1}H NMR spectra. For example, through the convergent approach, the "click chemistry" and azo-coupling reactions were used. Thus, 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 $\delta = 6.8$ ppm before (in **G1-S** and **G2-S**) and after (**G1-≡-S** and **G2-≡-S**) the azo-coupling reactions, the dendritic growth could be confirmed. On the other hand, the substitution of the chloride groups to azide groups and the "click chemistry" reaction were the typical reactions



Scheme 3. The synthesis of high-generation dendrons (**G3-S** to **G5-S**).

through the divergent approach. In the ^{1}H NMR spectrum of **G1-4N$_3$-S** (Figure S13, the Supporting Information) and **G2-8N$_3$-S** (Figure S17, the Supporting Information), the original peak at $\delta = 3.72$ ppm of chloromethyl groups in **G1-4Cl-S** (Figure S11, the Supporting Information) and **G2-8Cl-S** (Figure S15, the Supporting Information) disappeared, whereas the signal at $\delta = 3.60$ ppm was enhanced, indicating that the cores of dendrons have been synthesized successfully. For high-generation dendrons **G3-S** to **G5-S**, due to their large molecular weights, the peaks in their ^{1}H NMR spectra became broad, and the larger molecular weights resulted in even broader peaks. As shown in their ^{1}H NMR spectra (Figure S19, S21, S23, the Supporting Information), after the "click-chemistry" reaction, the signal at about $\delta = 3.6$ ppm, which can be assigned to the protons of -CH_2N$_3$, disappeared, whereas their characteristic peaks, such as about $\delta = 3.1$ ($-CH_2S-$), 4.5 ppm ($-COOCH_2-$), 6.7 (ArH) and so on, were still present, confirming the successful "click-chemistry" reaction. The structures of dendrimers **G1-S-GL** to **G4-S-GL** could be confirmed in the similar way. Figure 2 showed the ^{1}H NMR spectra of **G1-≡-S**, **G1-6N$_3$-S-GL**, and **G3-S-GL** as an example to illustrate the successful synthesis



Scheme 4. The synthesis of core **G1-6N$_3$-S-GL**.

of high-generation dendrimers. Besides this, the integration of the signals of ^{1}H NMR spectra was another piece of strong evidence to confirm the perfection of the high-generation dendrimers. We also took the ^{1}H NMR spectra of **G3-S-GL** as an example. As shown in Figure 2, the peaks at $\delta = 5.33$ ppm should be assigned to the protons of the methylene group linked to triazoles from the core **G1-6N$_3$-GL**, whereas the broad peaks at $\delta = 4.3$–4.7 ppm should be assigned to the protons of the methylene group linked to triazoles and ester groups from the dendrons. The integral ratio of these two peaks was 0.26:7.68, which was very similar to the theoretical value 1:28 (0.26:7.28). Thus, according to their integral ratio, the perfection of these high-generation dendrimers could be confirmed. A similar phenomenon was also observed in their ^{13}C NMR spectra. Still using **G3-S-GL** as an example, as shown in Figure 3, with the exception of some characteristic peaks of functional groups, the ^{13}C NMR spectra of **G1-≡-S**, **G1-6N$_3$-S-GL** and **G3-S-GL** were very similar, because they were all composed of sulfonyl-chromophore moieties and triazole groups. After the "click-chemistry" reaction, the peaks at $\delta = 70.1$, 81.6 (terminal alkynes, **G1-≡-S**), and 53.1 ppm (-CH_2N_3, **G1-6N$_3$-S-GL**) disappeared, whereas the peak corresponding to the ester groups from the end-capped dendrons ($\delta = 166.7$ ppm) was still present, again confirming the successful synthesis of high-generation dendrimers. In addition, the 2D NMR spectra (including H,H-COSY, C,C-COSY and HMBC spectra) of high-generation dendrimers were performed to further confirm the structures of high-generation dendrimers once more, and all gave satisfactory results. Figure 4 shows the NMR spectra of **G3-S-GL** as a representative example, whereas the other spectra are presented in the Supporting Information (Figures S39–S47).

MALDI-TOF-MS proved to be a good method to confirm the exact molecular weights of the dendrimers. Figures S48–S61 (the Supporting Information) showed the MALDI-TOF-MS spectra of the obtained dendrimers, and all the experimental results were in good agreement with the expected molecular weights for the structures. However, the MALDI-TOF-MS spectra of the azide-containing dendrimers did not give clear signals, which could be caused by fragment ions arising due to the fragmentation of unstabilized azide groups during the MALDI analysis. For example, in the MALDI-TOF-MS spectrum of **G1-4N$_3$-S** (Figure S53, the Supporting Information), except for the peaks at *m/z* 1184.7 ($[M+\mathrm{Na}]^+$) and 1162.7 ($[M+\mathrm{H}]^+$), there was only one other apparent peak at 1134.6 ($[M+\mathrm{H}-28]^+$), possibly due to one of the four azide groups that had degraded to nitrene. Unfortunately, we failed to detect any signals within the appropriate mass range for high-generation dendrimers **G4-S**, **G5-S**, and **G4-S-GL**, and the possible reason might be that their larger molecular weight resulted in much lower peak intensity. In fact, the MALDI-TOF-MS spectrum of **G3-S-GL** (Figure S61, the Supporting Information), with much lower molecular weight than **G4-S-GL**, was still unclear. Alternatively, the laser light-scattering (LLS) measurement was conducted to evaluate their absolute molecular weights. As shown in Table 1, the tested values of these dendrimers were similar to (or a little higher than) the calculated values, confirming their structures again. Meanwhile, the gel permeation chro-

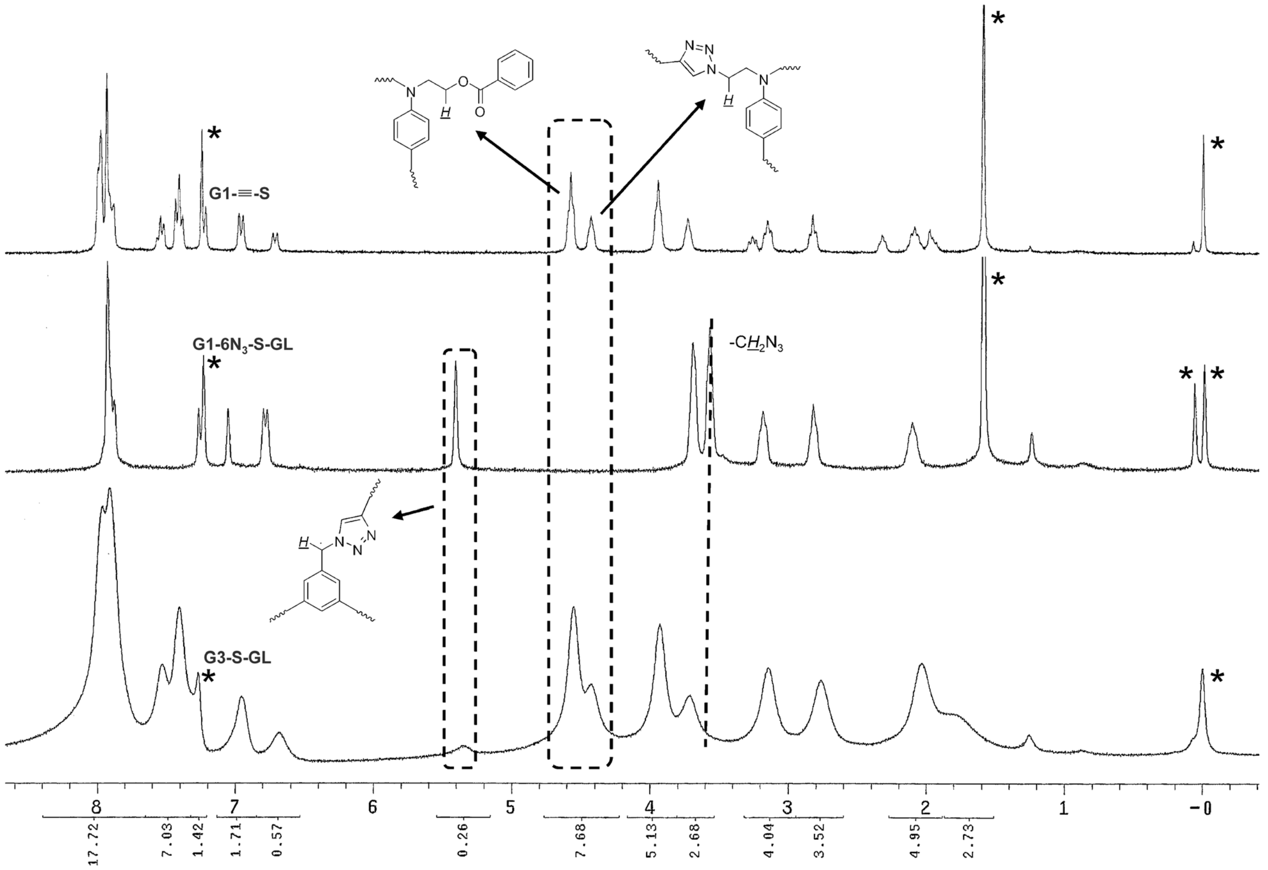


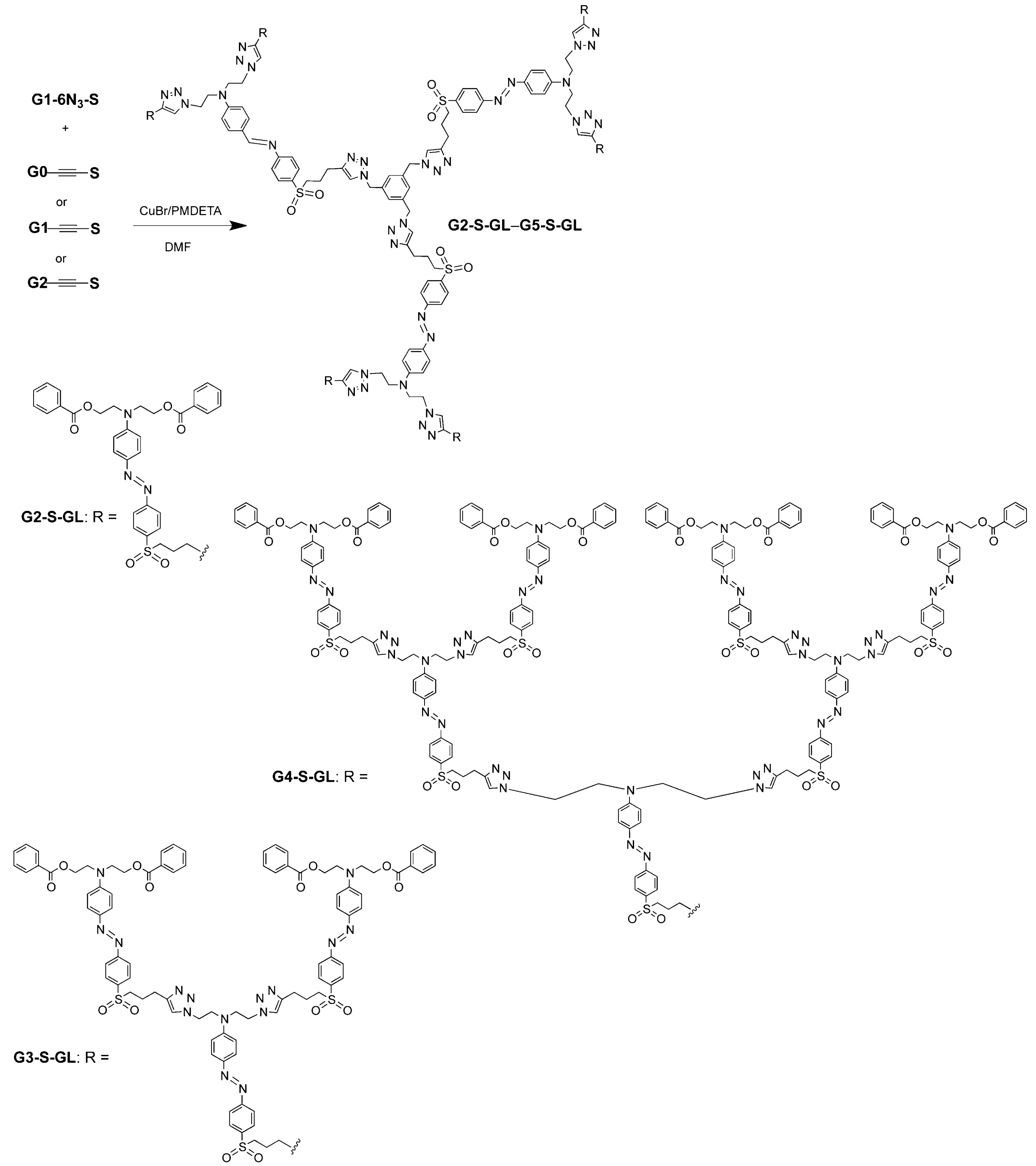
Figure 2. ^{1}H NMR spectra of **G1-≡-S**, **G1-6N$_3$-S-GL** and **G3-S-GL** in CDCl$_3$ (the peaks from residual solvents, water, and TMS were marked with *).

Table 1. Molecular-weight-tested data of dendrimers.

Compound	M_w[a]	M_w/M_n[a]	m/z[b]	M_w[c]	m/z (calcd)	M_c/M_w[f]
G1-S	1510	1.03	1501.5	2020	1501.7[d]	0.979
G2-S	3800	1.05	3679	5550	3680[d]	0.962
G3-S	6060	1.04	8038	12100	8036[d]	1.322
G4-S	9340	1.04	–[g]	19200	16728[e]	1.791
G5-S	12200	1.08	–[g]	41200	34152[e]	2.799
G1-S-GL	2160	1.05	2135.4	3650	2135.7[d]	0.978
G2-S-GL	4840	1.03	5406	6800	4505[d]	0.926
G3-S-GL	8150	1.10	11954	14300	11941[d]	1.465
G4-S-GL	11800	1.07	–[g]	34600	24989[e]	2.118
G5[h]	30300	1.36			33966	1.121
G3-TPA[h]	14850	1.09			24813	1.672

[a] Determined by GPC in THF on the basis of a polystyrene calibration. [b] Measured by MALDI-TOF mass spectroscopy. [c] Determined by LLS technique. [d] Calculated for $[M+\text{Na}]^+$. [e] Calculated for $[M]^+$. [f] M_c was the calculated molecular weight. [g] Not obtained. [h] Tested in our previous work, ref. [8].

matography (GPC) measurement was also conducted. All the GPC curves of the dendrimers showed narrow peaks with polydispersity indexes (PDI) of less than 1.10 (Table 1), indicating that the products possessed monodispersed molecular weights. Meanwhile, the increasing trend in the tested GPC results was also consistent with the actual molecular weights. In fact, GPC was one type of size exclusion chromatography in essence, and its mechanism to test the relative molecular weights of polymers should be that the efflux time of polymers with different molecular weight should be different, since their size in dilute solution is different. However, the molecular weight was not the only factor to affect the hydrodynamic radius of polymers. For example, for the same molecular weight, the hydrodynamic radius of dendritic structures should be much smaller than the linear structures, and the hydrodynamic radius of the dendritic structures with spherical shape should be the smallest one. Therefore, GPC analysis, using linear polystyrenes as calibration standards, often underestimates the molecular weights of dendrimers with a 3D branched structure,[13] thus, the tested molecular weights of higher-generation dendrimers were all lower than their true values. Here, by the utilization of this special feature, the GPC results might be used to characterize the 3D branched structure of dendrimers in some sense: if the difference between the tested and true values was higher, its hydrodynamic radius should be more different from that of linear polymers, and its topological structure should be much closer to spherical. A M_c/M_w value (in which M_c is the calculated molecular weight, whereas M_w is the weight average molecular weight determined by GPC) was used to describe this difference and the values were listed in Table 1. As expected, accompanied with the generation increase of dendrimers, the M_c/M_w values also increases, and the topology of the 3D branched



Scheme 5. The synthesis of dendrimers (**G1-S-GL** to **G4-S-GL**).

structures was improved. Also, the M_c/M_w values of high-generation dendrimers were higher than normal dendrons of the same generation (for example: the M_c/M_w value of **G4-S-GL** was 2.118, but for **G4-S** the value was 1.791), indicating that the topological structure of dendrimers should be better than the normal dendrons, and further confirming our previous idea on dendrimers in NLO fields. More excitingly, when the molecular weights were similar, the M_c/M_w values of these sulfonyl-chromophore-based dendrimers were all higher than their nitro-chromophore-based counterparts (for example: the M_c/M_w value of **G5-S** was 2.799, whereas only 1.121 for **G5**). This result indicated that the 3D topological structure of these sulfonyl-chromophore-based dendrimers should be better than that of nitro-based ones in our previous work, which should be very beneficial to their NLO effect; this point was unexpected at the very beginning of this work.

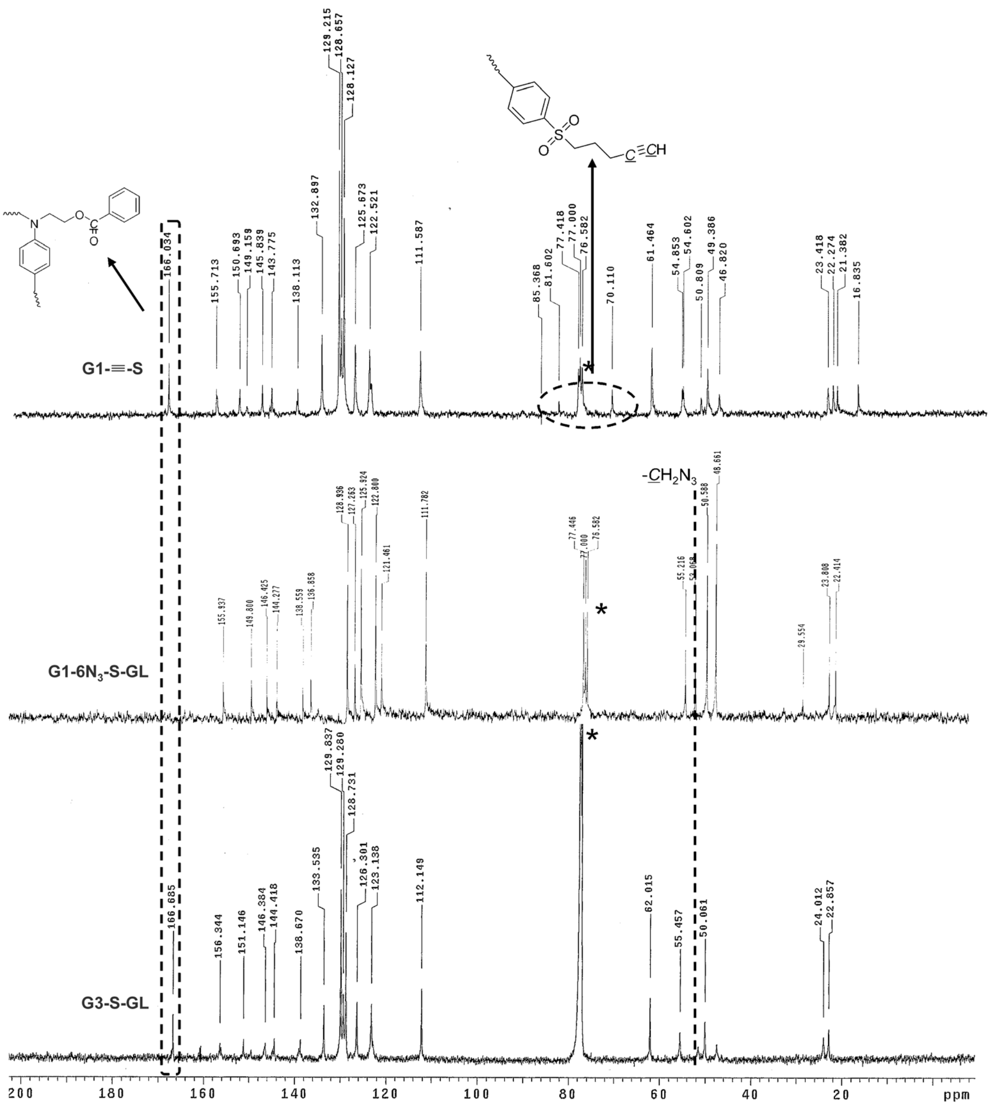


Figure 3. ^{13}C NMR spectra of **G1-≡-S**, **G1-6N$_3$-S-GL** and **G3-S-GL** in CDCl$_3$ (the peaks from residual solvents were marked with *).

As mentioned above, the original idea of this paper was the usage of the sulfonyl chromophore, to improve the optical transparency and the stability of NLO dendrimers. To evaluate the optical transparency of these dendrimers, their UV/Vis spectra (Figure 5 and the Supporting Information, S62–S72 and Table S1) in different solvents were tested. The maximum absorption wavelengths (λ_{max}) for the π–π* transition of the azo moieties in films are listed in Table 2. Excitingly, in comparison with the nitro-chromophore-based dendrimers, the λ_{max} values of all the dendrimers in this paper were blueshifted by about 35 nm, demonstrating much better optical transparency, which could contribute much to their practical applications in photonics fields. Meanwhile, accompanying with the generation increase of dendrimers, the λ_{max} was further blueshifted, due to more perfect 3D structures of higher-generation dendrimers. However, since these sulfonyl-chromophore-based dendrimers have better 3D topological structures than the nitro-based chromophore dendrimers, the differences of λ_{max} between low-generation- and high-generation dendrimers were not so obvious as in the nitro-based ones (for example: a blueshift of 12 nm from **G2** to **G5**, but only 2 nm from **G2-S** to **G5-S**).

Table 2. The maximum absorption of dendrimers in films.

Compound	λ_{max} [nm]	Compound	λ_{max} [nm]
G1-S	438	**G1**	479[a]
G2-S	434	**G2**	482[a]
G3-S	433	**G3**	480[a]
G4-S	432	**G4**	470[a]
G5-S	432	**G5**	470[a]
G1-S-GL	436	**G1-TPA**	470[a]
G2-S-GL	434	**G2-TPA**	470[a]
G3-S-GL	433	**G3-TPA**	470[a]
G4-S-GL	433		

[a] Tested in our previous work, ref. [8].

These dendrimers were thermally stable (Figure S73 and S74, the Supporting Information), with their 5 % weight loss temperatures listed in Table 3. The glass transition tempera-

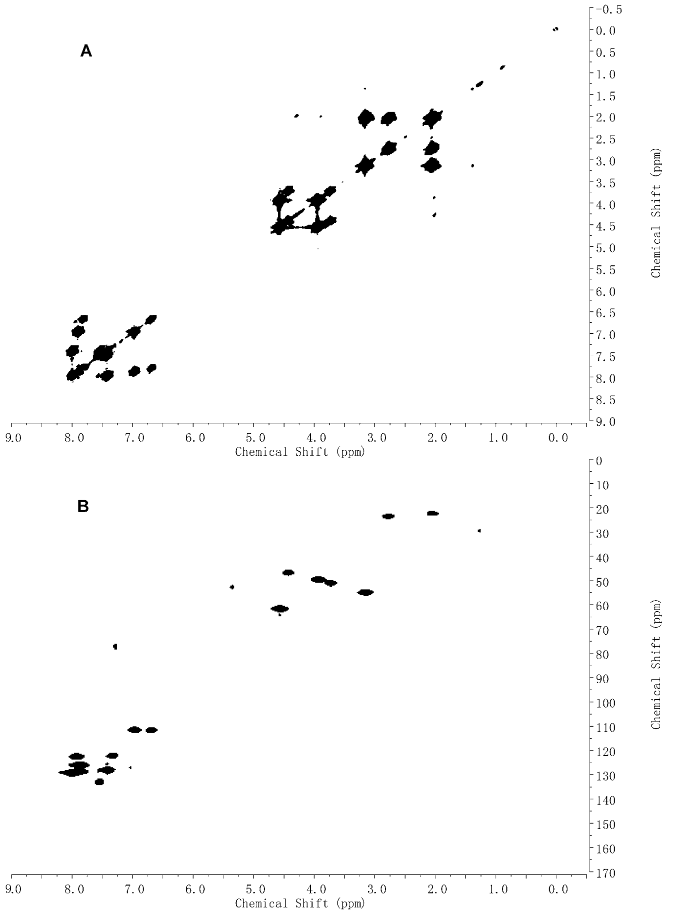


Figure 4. 2D NMR spectra of **G3-S-GL** in $CDCl_3$. A) H,H-COSY; B) C,H-COSY).

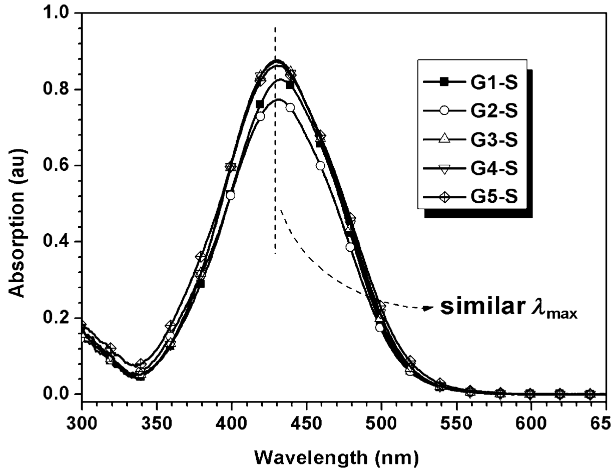


Figure 5. UV/Vis spectra of THF solutions of dendrimers **G1-S** to **G5-S** (0.02 $mg\,mL^{-1}$).

tures (T_g) of the dendrimers were also investigated by using differential scanning calorimetry (DSC), with the results summarized in Table 3. Similar to **G1** to **G5** and **G1-TPA** to **G3-TPA**, the growth of the NLO dendrimers in this paper also resulted in the increase of T_g values. Due to the special main-chain structure of the sulfonyl-chromophore moieties in these dendrimers, the thermally stabilities of **G1-S** to **G5-S** and **G1-S-GL** to **G4-S-GL** were improved relative to the nitro-chromophore-based dendrimers. Considering that the stability of the NLO effect was associated with the glass transitions, the higher T_g values should benefit to their stability in the practical applications.

Table 3. The thermal properties of dendrimers.

Compound	T_g[a] [°C]	T_d[b] [°C]	Compound	T_g [°C]	T_d [°C]
G1-S	–[c]	311	**G1**[d]	56	300
G2-S	119	314	**G2**[d]	76	295
G3-S	126	313	**G3**[d]	90	278
G4-S	134	304	**G4**[d]	117	262
G5-S	156	295	**G5**[d]	125	275
G1-S-GL	71	281	**G1-TPA**[d]	62	280
G2-S-GL	117	308	**G2-TPA**[d]	74	292
G3-S-GL	–[c]	299	**G3-TPA**[d]	92	286
G4-S-GL	138	293			

[a] Glass transition temperature (T_g) of polymers detected by the DSC analyses under argon at a heating rate of 10 °C min^{-1}. [b] 5 % weight loss temperature of polymers detected by TGA analyses under nitrogen at a heating rate of 10 °C min^{-1}. [c] Not obtained. [d] Tested in our previous work in ref. [8].

NLO properties: The NLO effect was the most important parameter for NLO materials. If the NLO effects of these dendrimers were not satisfied, then improved properties of optical transparency and stability were meaningless. To evaluate the NLO activity of these dendrimers, their poled thin-films were prepared. The most convenient technique to study the second-order NLO activity is to investigate the second harmonic generation (SHG) processes characterized by d_{33}, an SHG coefficient. The method for the calculation of the SHG coefficients (d_{33}) for the poled films has been reported in our previous papers.[6–8,10] From the experimental data, the d_{33} values of the dendrimers were calculated at a fundamental wavelength of 1064 nm (Table 4). To check the reproducibility, we repeated the measurements at least three times and almost got the same results. However, during the poling procedure, the thin films of **G4-S-GL** were always

Table 4. NLO results of dendrimers.

	T_e[a] [°C]	l_s[b] [μm]	d_{33}[c] [pm V^{-1}]	$d_{33(\infty)}$[d] [pm V^{-1}]	Φ[e]	N[f]
G1-S	70	0.27	52	14	0.11	0.467
G2-S	120	0.24	72	20	0.18	0.567
G3-S	130	0.25	103	29	0.20	0.604
G4-S	140	0.19	117	33	0.23	0.620
G5-S	165	0.21	133	38	0.31	0.627
G1-S-GL	65	0.27	107	29	0.19	0.490
G2-S-GL	125	0.18	136	38	0.29	0.578
G3-S-GL	130	0.22	181	51	0.33	0.609

[a] The best poling temperature. [b] Film thickness. [c] Second harmonic generation (SHG) coefficient. [d] The nonresonant d_{33} values calculated by using the approximate two-level model. [e] Order parameter $\Phi = 1 - A_1A_0^{-1}$, A_1 and A_0 are the absorbance of the polymer film after and before poling, respectively.[f] The loading density of the effective chromophore moieties.

broken by the DC electric field, and therefore, its d_{33} value was not obtained. The reason for this is unclear at present.

Similar to our previous case on the nitro-chromophore-based dendrimers, the d_{33} values increased from **G1-S** (52 pm V^{-1}) to **G5-S** (133 pm V^{-1}), accompanied with the increasing loading density of the chromophore moieties, and the higher the generation of dendrons, the higher the d_{33} values. Due to the more ideal 3D branched topological structure, the dendrimers demonstrated much higher d_{33} values than the normal ones. In particular, the high generation dendrimer **G3-S-GL**, its d_{33} value was up to 181 pm V^{-1}, which should be, to the best of our knowledge, the highest value so far for polymers containing the sulfonyl-based chromophore moieties. Compared with the nitro-chromophore-based dendrimers (the d_{33} value of **G5** was 193.1 pm V^{-1}, whereas it was 246.0 pm V^{-1} for **G3-TPA**), it seems that the NLO coefficients of the sulfonyl-chromophore-based dendrimers possessed no advantage. However, this was not the case, and it may be due to the different resonant enhancement effects at 532 nm (double the frequency of the 1064 nm fundamental wavelength) of these two types of dendrimers, for their different optical transparency.[14] Therefore, by using the approximate two-level model, we calculated their nonresonant d_{33} values, and the results were summarized in Table 4 ($d_{33(\infty)}$ values). Because of the much better optical transparency of the sulfonyl-chromophore-based dendrimers, their $d_{33(\infty)}$ values were still very high. For example, the $d_{33(\infty)}$ value of **G5-S** was 38 pm V^{-1}, and the $d_{33(\infty)}$ value of **G3-S-GL** was even up to 51 pm V^{-1}, higher than their corresponding nitro-chromophore-based counterparts (the $d_{33(\infty)}$ value of **G5** is 34 pm V^{-1}, whereas it is 43 pm V^{-1} for **G3-TPA**). Considering that the d_{33} value of the same NLO polymer could be different when measured by different methods or different testing systems, even at different times, and the $d_{33(\infty)}$ value was calculated by the approximate two-level model, it was not so convincing to say "the NLO coefficients of these sulfonyl-chromophore-based dendrimers were higher than their corresponding nitro-chromophore-based ones". However, at least, we could draw a conclusion: the NLO coefficients of these sulfonyl-chromophore-based dendrimers were at least on the same level to their corresponding nitro-chromophore-based counterparts.

To further explore the alignment of the chromophore moieties in these dendrimers, we measured their order parameter (Φ; Table 4 and Figure S75–S82). By using the relation of $\Phi = 1 - A_1A_0^{-1}$, the Φ values of the dendrimers were calculated, with the results listed in Table 4. The trend of the Φ values was the same as the d_{33} values of dendrimers, confirming that higher generation and increasingly 3D branched topological structure, led to the better alignment of the chromophore moieties under the poling process, and thus to better NLO performance.

To further confirm the better stability of these dendrimers than the nitro-chromophore-based ones, the depoling experiments of poled films of these dendrimers were conducted, in which the real-time decays of their SHG signals were monitored as the poled films were heated from 40 to 160 °C in air at a rate of 4 °C min^{-1}. Figure 6 displays the decay of the SHG coefficient of **G3-S** to **G5-S** and **G3-S-GL** as a function of temperature. As expected, all of them demonstrated higher stability than the nitro-chromophore-based dendrimers. For example, the onset temperatures for decays (T_{onset}) in the d_{33} values of **G5-S** was up to 123 °C, whereas only 107 °C for **G5**. And this should be ascribed to the special main-chain structure of the sulfonyl-based chromophore moieties in these dendrimers as mentioned above.

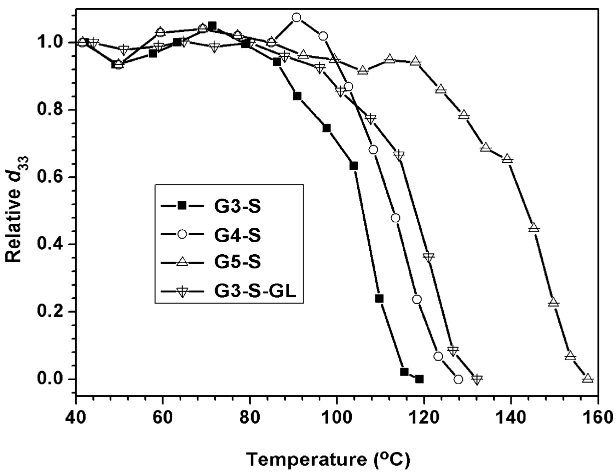


Figure 6. Decay curves of the SHG coefficients of dendrimers as a function of the temperature.

Conclusion

By using a combination of divergent and convergent approaches, two series of the sulfonyl-chromophore-based high-generation NLO dendrimers, **G1-S** to **G5-S** and **G1-S-GL** to **G4-S-GL**, were successfully obtained through the powerful "click-chemistry" reaction. Compared with the corresponding nitro-chromophore-based dendrimers, there were at least two advantages of these sulfonyl-chromophore-based analogues: much better optical transparency derived from the lower μ value of the sulfonyl chromophore and the much higher stability from the special main-chain structure of the sulfonyl-chromophore moieties in these dendrimers. Meanwhile, thanks to the perfect three-dimensional (3D) spatial isolation from the highly branched structure, large NLO coefficients were still achieved, and the d_{33} value for **G3-S-GL** of 181 pm V^{-1}, to the best of our knowledge, should be the highest one so far reported for the polymers containing the sulfonyl-chromophore moieties.

Experimental Section

Materials and instrumentation: Tetrahydrofuran (THF) was dried over and distilled from a K/Na alloy under an atmosphere of dry nitrogen. *N,N*-Dimethylform amide (DMF) was dried over and distilled from CaH_2

under an atmosphere of dry nitrogen. Compound **S1**, **S2**, and **S3** have been already prepared in our previous work.[7a,b] *N,N,N,N,N*-Pentamethyldiethylenetriamine (PMDETA) and 1,3,5-tris(bromomethyl)benzene (**S4**) 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, Varian Mercury600 or Bruker ARX 400 spectrometer. H,H COSY and C,H COSY spectra of high generation dendrimers were measured on a 600 MHz Bruker Avance III NMR Spectrometer with a CryOProbe. The Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer-2 spectrometer in the region of 3000–400 cm^{-1}. UV/Visible spectra were obtained using a Shimadzu UV-2550 spectrometer. Matrix-assisted laser desorption ionization time-of-flight mass spectra (MALDI-TOF MS) were measured on a Voyager-DE-STR MALDI-TOF mass spectrometer (ABI, American) equipped with a 337 nm nitrogen laser and a 1.2 m linear flight path in positive ion mode. Elemental analyses (EA) were performed by a CARLOERBA-1106 micro-elemental analyzer. Gel permeation chromatography (GPC) was used to determine the molecular weights of polymers. GPC analysis was performed on a Waters HPLC system equipped with a 2690D separation module and a 2410 refractive index detector. Polystyrene standards were used as calibration standards for GPC. THF was used as an eluent, and the flow rate was 1.0 mL min^{-1}. Thermal analysis was performed on NETZSCH STA449C thermal analyzer at a heating rate of 10 °C min^{-1} in nitrogen at a flow rate of 50 cm^3 min^{-1} for thermogravimetric analysis (TGA). The thermal transitions of the polymers were investigated using a METTLER differential scanning calorimeter DSC822e under nitrogen 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 with an Ambios Technology XP-2 profilometer.

Synthesis of dendrimer G1-S: Chromophore **G0-≡-S** (823.3 mg, 1.32 mmol), *N,N*-bis(2-azidoethyl)aniline (**S1**) (138.8 mg, 0.60 mmol), CuSO$_4$·5H$_2$O (10 mol %), NaHCO$_3$ (20 mol %), and ascorbic acid (20 mol %) were dissolved in THF (24 mL)/H$_2$O (6 mL) under nitrogen in a Schlenk flask. After the mixture was stirred at 25–30 °C under nitrogen atmosphere for 3 h, the reaction was terminated by the addition of water, and then extracted with chloroform, and washed with brine. The organic layer was dried over anhydrous magnesium sulfate and purified by column chromatography using ethyl acetate/chloroform (2:1, v/v) as eluent to afford an orange solid **G1-S** (840.8 mg, 94.8 %). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ = 2.08 (m, 4H, -CH$_2$-), 2.80 (t, J = 6.3 Hz, 4H, -CH$_2$C-), 3.15 (t, J = 6.9 Hz, 4H, -SCH$_2$-), 3.63 (s, br, 4H, -NCH$_2$-), 3.95 (s, br, 8H, -NCH$_2$-), 4.35 (s, br, 4H, -NCH$_2$-),4.59 (s, br, 8H, -COOCH$_2$-), 6.62 (d, J = 7.5 Hz, 2H, ArH), 6.81 (t, J = 8.1 Hz, 1H, ArH), 6.97 (d, J = 7.5 Hz, 4H, ArH), 7.14 (s, 2H, C=CH), 7.25 (m, 2H, ArH), 7.40 (m, 8H, ArH), 7.56 (m, 4H, ArH), 7.9–8.10 ppm (m, 20H, ArH); ^{13}C NMR (75 MHz, CDCl$_3$, 298 K): δ = 22.47, 23.64, 47.21, 49.61, 51.34, 55.08, 61.60, 111.78, 112.79, 118.37, 122.10, 122.68, 125.84, 128.30, 128.85, 129.41, 129.66, 133.07, 138.39, 144.05, 145.53, 145.78, 150.77, 155.94, 166.23 ppm; IR (KBr): $\tilde{\nu}$ = 1711 (C=O), 1316, 1130 cm^{-1} (-SO$_2$-); MALDI-TOF MS *m/z* calcd for ($C_{80}H_{79}N_{13}O_{12}S_2$): 1501.7 [$M$+Na]$^+$; found: 1501.5; elemental analysis calcd (%) for $C_{80}H_{79}N_{13}O_{12}S_2$: C 64.98, H 5.38, N 12.31; found: C 64.58, H 5.61, N, 12.35.

Synthesis of dendrimer G1-≡-S: Diazonium salt **S2** (241.6 mg, 0.75 mmol) and dendrimer **G1-S** (739.0 mg, 0.50 mmol) were dissolved in DMF (10 mL)/THF (5 mL) at 0 °C. The reaction mixture was stirred for 40 h at 0 °C, then treated with H$_2$O and extracted with CHCl$_3$, washed with brine. The organic layer was dried over anhydrous sodium sulfate. After removal the organic solvent, the crude product was purified by column chromatography on silica gel using ethyl acetate/chloroform (2:1, v/v) as eluent to afford orange solid **G1-≡-S** (670.4 mg, 78.3 %). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ = 1.96 (m, 3H, -CH$_2$- and C≡CH), 2.10 (m, 2H, -CH$_2$-), 2.33 (s, br, 2H, -CH$_2$-), 2.83 (t, 4H, -CH$_2$-), 3.15 (t, 4H, -SCH$_2$-), 3.27 (t, J = 6.9 Hz, 2H, -SCH$_2$-), 3.74 (br, s, 4H, -NCH$_2$-), 3.96 (br, s, 8H, -NCH$_2$-), 4.44 (s, br, 4H, -NCH$_2$-), 4.59 (s, br, 8H, -COOCH$_2$-), 6.73 (d, J = 8.4 Hz, 2H, ArH), 6.98 (d, J = 9.0 Hz, 4H, ArH), 7.23 (s, 2H, C=CH), 7.43 (t, J = 7.8 Hz, 8H, ArH), 7.54 (t, J = 6.3 Hz, 8H, ArH), 7.9–8.1 ppm (m, 20H, ArH); ^{13}C NMR (75 MHz, CDCl$_3$, 298 K): δ = 16.84, 21.38, 22.27, 23.42, 46.82, 49.39, 50.81, 54.60, 54.85, 61.46, 70.11, 81.60, 85.37, 111.59, 122.52, 125.67, 128.13, 128.66, 129.22, 132.90, 138.11, 143.78, 145.84, 149.16, 150.69, 155.71, 166.03 ppm; IR (KBr): $\tilde{\nu}$ = 3289 (C≡CH), 1716 (C=O), 1316, 1132 cm^{-1} (-SO$_2$-); MALDI-TOF MS: *m/z* calcd (%) for $C_{91}H_{89}N_{15}O_{14}S_3$: 1734.6 [$M$+Na]$^+$; found: 1734.1.

Synthesis of dendrimer G2-S: The procedure was similar to the synthesis of dendrimer **G1-S** but using dendrimer **G1-≡-S** (450.0 mg, 0.263 mmol) and **S1** (27.7 mg, 0.119 mmol). The crude product was purified by column chromatography on silica gel using THF/chloroform (1:1, v/v) as eluent to afford orange solid **G2-S** (291.2 mg, 66.9 %). ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ = 2.08 (m, -CH$_2$-), 2.77 (m, -CH$_2$C-), 3.15 (s, br, -SCH$_2$-), 3.62 (s, br, -NCH$_2$-), 3.73 (s, br, -NCH$_2$-), 3.94 (t, J = 8.0 Hz, -NCH$_2$-), 4.35 (s, br, -NCH$_2$-), 4.43 (s, br, -NCH$_2$-), 4.59 (t, J = 8.0 Hz, -COOCH$_2$-), 6.60 (d, J = 8.0 Hz, ArH), 6.71 (d, J = 8.0 Hz, ArH), 6.79 (s, ArH), 6.96 (d, J = 8.0 Hz, ArH), 7.13 (s, C=CH), 7.40 (m, ArH), 7.56 (m, ArH), 7.9–8.1 ppm (m, ArH); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K): δ = 22.64, 23.78, 47.26, 47.61, 49.85, 55.24, 61.80, 78.26, 109.99, 110.01, 111.99, 115.86, 122.92, 126.06, 129.05, 133.30, 138.54, 144.28, 147.96, 150.99, 156.19, 166.48 ppm; IR (KBr), $\tilde{\nu}$ = 1716 (C=O), 1316, 1131 cm^{-1} (-SO$_2$-); MALDI-TOF MS: *m/z* calcd for $C_{192}H_{191}N_{37}O_{28}S_6$: 3680 [$M$+Na]$^+$; found: 3679; elemental analysis calcd (%) for $C_{192}H_{191}N_{37}O_{28}S_6$: C 63.06, H 5.26, N 14.17; found: C 62.41, H 5.34, N 13.91.

Synthesis of dendrimer G2-≡-S: The procedure was similar to the synthesis of dendrimer **G1-≡-S** but using diazonium salt **S2** (64.4 mg, 0.20 mmol) and dendrimer **G2-S** (182.9 mg, 0.050 mmol). The reaction time was 5 days. The crude product was purified by column chromatography on silica gel using THF/chloroform (1:1, v/v) as eluent to afford orange solid **G2-≡-S** (143.2 mg, 73.6 %). ^{1}H NMR (400 MHz, CDCl$_3$, 298 K), δ (TMS, ppm): 2.08 (m, -CH$_2$- and C≡CH), 2.80 (m, -CH$_2$C-), 3.15 (m, -SCH$_2$-), 3.73 (s, br, -NCH$_2$-), 3.94 (m, -NCH$_2$-), 4.43 (s, br, -NCH$_2$-), 4.59 (t, J = 8.0 Hz, -COOCH$_2$-), 6.69 (d, J = 8.0 Hz, ArH), 6.97 (d, J = 8.0 Hz, ArH), 7.22 (s, C=CH), 7.41 (m, ArH), 7.56 (m, ArH), 7.9–8.1 ppm (m, ArH); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K): δ = 17.24, 21.75, 23.46, 29.22, 33.32, 45.18, 47.26, 49.83, 55.25, 61.83, 67.28, 67.59, 70.40, 80.48, 98.34, 101.77, 107.90, 110.00, 111.99, 122.55, 122.91, 124.77, 126.06, 129.61, 133.30, 138.51, 144.24, 146.26, 149.42, 151.02, 156.16, 166.48 ppm; IR (KBr): $\tilde{\nu}$ = 3286 (C≡CH), 1716 (C=O), 1316, 1132 cm^{-1} (-SO$_2$-); MALDI-TOF MS: *m/z* calcd for $C_{203}H_{201}N_{39}O_{30}S_7$: 3914 [$M$+Na]$^+$; found: 3914.

Synthesis of dendrimer G1-4Cl-S: The procedure was similar to the synthesis of dendrimer **G1-S** but using chromophore **S3** (497.6 mg, 1.10 mmol) and *N,N*-bis(2-azidoethyl)aniline (**S1**; 115.6 mg, 0.50 mmol). The crude product was purified by column chromatography on silica gel using pure acetate as eluent to afford orange solid **G1-4Cl-S** (514.1 mg, 90.5 %). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K), δ = 2.08 (m, 4H, -CH$_2$-), 2.81 (br, s, 4H, -CH$_2$C-), 3.16 (br, s, 4H, -SCH$_2$-), 3.64 (br, s, 4H, -NCH$_2$-), 3.72 (br, s, 8H, -CH$_2$Cl-), 3.86 (br, s, 8H, -NCH$_2$-), 4.35 (br, s, 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): δ = 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): $\tilde{\nu}$ = 1316, 1131 cm^{-1} (-SO$_2$-); MALDI-TOF MS: *m/z* calcd for $C_{52}H_{59}N_{13}O_4S_2Cl_4$: 1159.0 [$M$+Na]$^+$; found: 1158.5.

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 reaction was allowed to stir at 80 °C for 12 h and then the solution was poured into a large amount of water. The precipitate was collected and washed several times with water and methanol/water (1:1) and then dried under vacuum to afford orange solid (275 mg, 94.6 %). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ = 2.07 (m, 4H, -CH$_2$-), 2.80 (br, s, 4H, -CH$_2$C-), 3.16 (t, J = 7.8 Hz, 4H, -SCH$_2$-), 3.60 (br, s, 8H, -CH$_2$N$_3$-), 3.69 (br, s, 4H, -NCH$_2$-), 4.35 (br, s, 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): δ = 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$_3$), 1316, 1131 cm^{-1} (-SO$_2$-);

MALDI-TOF MS: *m/z* calcd for $C_{52}H_{59}N_{25}O_4S_2$: 1184.5 $[M+Na]^+$; found: 1184.7.

Synthesis of dendrimer G2-8Cl-S: The procedure was similar to the synthesis of dendrimer **G1-S**, but using chromophore **S3** (199.1 mg, 0.44 mmol) and **G1–4N$_3$-S** (116.2 mg, 0.10 mmol). The crude product was purified by column chromatography on silica gel by using THF/chloroform (1:1) as eluent to afford orange solid **G2-8Cl-S** (276.0 mg, 92.9 %). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ = 1.6–1.9 (-CH$_2$-), 2.0–2.2 (-CH$_2$-), 2.79 (br, s, -CH$_2$C-), 3.14 (br, s, -SCH$_2$-), 3.62 (br, s, -NCH$_2$-), 3.71 (br, s, -NCH$_2$-), 3.86 (br, s, -CH$_2$Cl-), 3.94 (br, s, -NCH$_2$-), 4.36 (br, s, -NCH$_2$-), 4.43 (br, s, -NCH$_2$-), 6.62 (br, s, ArH), 6.76 (d, *J* = 7.8 Hz, ArH), 6.79 (d, *J* = 8.4 Hz, ArH), 7.15 (s, C=CH), 7.8–8.1 ppm (ArH); ^{13}C NMR (75 MHz, CDCl$_3$, 298 K): δ = 22.54, 23.67, 27.69, 40.21, 47.09, 51.13, 53.25, 55.12, 68.44, 107.54, 111.62, 112.83, 122.41, 122.87, 125.98, 128.95, 129.80, 138.60, 144.32, 146.12, 149.62, 155.90 ppm; IR (KBr): $\tilde{\nu}$ = 1316, 1131 cm^{-1} (-SO$_2$-); MALDI-TOF MS: *m/z* calcd for $C_{136}H_{151}Cl_8N_{37}O_{12}S_6$: 2994 $[M+Na]^+$; found: *m/z* 2993.

Synthesis of dendrimer G2-8N$_3$-S: The procedure was similar as the synthesis of dendrimer **G1-4N$_3$-S** but using **G2-8Cl-S** (178.0 mg, 0.060 mmol) and NaN$_3$ (62.4 mg, 0.96 mmol). The crude product was purified by column chromatography on silica gel using THF/chloroform (1:1) as eluent to afford orange solid **G2-8N$_3$-S** (127.6 mg, 66.4 %). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ = 1.4–1.6 (-CH$_2$-), 2.08 (s, br, -CH$_2$-), 2.81 (br, s, -CH$_2$C-), 3.14 (br, s, -SCH$_2$-), 3.59 (br, s, -CH$_2$N$_3$-), 3.71 (br, s, -NCH$_2$-), 4.34 (br, s, -NCH$_2$-), 4.44 (br, s, -NCH$_2$-), 6.63 (br, s, ArH), 6.72 (br, s, ArH), 6.81 (d, *J* = 8.7 Hz, ArH), 7.14 (s, C=CH), 7.8–8.1 ppm (ArH); ^{13}C NMR (75 MHz, CDCl$_3$, 298 K): δ = 22.50, 23.67, 47.27, 48.63, 50.53, 55.13, 111.81, 112.93, 122.80, 125.93, 128.91, 138.53, 144.22, 145.81, 146.09, 149.22, 149.89, 155.94 ppm; IR (KBr): $\tilde{\nu}$ = 2096 (-N$_3$), 1316, 1130 cm^{-1} (-SO$_2$-); MALDI-TOF MS: *m/z* calcd for $C_{136}H_{151}N_{61}O_{12}S_6$: 3047 $[M+Na]^+$; found: 3045.

General procedure for the synthesis of G3-S, G4-S, and G5-S: A mixture of **G2-8N$_3$-S** (1.00 equiv), different end-capped dendrons (9.00 equiv), and CuBr (8.00 equiv) were dissolved in DMF (0.02 M-N$_3$) under nitrogen in a Schlenk flask, then *N,N,N,N,N*-pentamethyldiethylenetriamine (PMDETA) (8.00 equiv) was added. After the mixture was stirred at 25–30 °C for 6 h, the reaction was stopped by addition of water. The precipitate was purified by repeating precipitations of their THF or CHCl$_3$ solutions into ethyl acetate or acetone, and then filtered and washed with lots of ethyl acetate or acetone, dried in vacuum at 40 °C to a constant weight.

G3-S: According to the general procedure using compound **G2-8N$_3$-S** (30.2 mg, 0.010 mmol) and **G0-≡-S** (56.1 mg, 0.090 mmol). **G3-S** was obtained as orange powder (66.0 mg, 82.4 %). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ = 1.6–1.9 (-CH$_2$-), 2.0–2.2 (-CH$_2$-), 2.7–2.9 (-CH$_2$C- and -CH$_2$-), 3.1–3.3 (-SCH$_2$-), 3.6–3.8 (-NCH$_2$-), 3.8–4.0 (-NCH$_2$-), 4.3–4.5 (-OCH$_2$-), 4.5–4.7 (-COOCH$_2$-), 6.6–6.8 (ArH), 6.9–7.0 (ArH), 7.2–7.6 (ArH and C=CH), 7.8–8.1 ppm (ArH); ^{13}C NMR (150 MHz, CDCl$_3$, 298 K): δ = 22.67, 23.84, 47.29, 49.86, 51.25, 55.27, 61.83, 111.95, 122.96, 126.11, 128.56, 129.10, 129.65, 133.35, 138.46, 144.22, 150.96, 156.17, 166.51 ppm; IR (KBr): $\tilde{\nu}$ = 1316, 1716 (C=O), 1130 cm^{-1} (-SO$_2$-); MALDI-TOF MS: *m/z* calcd for $C_{416}H_{415}N_{65}O_{60}S_{14}$: 8036 $[M+Na]^+$; found: 8038; elemental analysis calcd (%) for $C_{416}H_{415}N_{65}O_{60}S_{14}$: C 62.35; H 5.22; N 14.86; found: C 62.04; H 5.88; N 14.68.

G4-S: According to the general procedure using compound **G2-8N$_3$-S** (18.1 mg, 0.006 mmol) and **G1-≡-S** (92.5 mg, 0.054 mmol). **G4-S** was obtained as orange powder (78.1 mg, 78.0 %). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ = 1.6–1.9 (-CH$_2$-), 2.0–2.2 (-CH$_2$-), 2.6–2.9 (-CH$_2$C- and -CH$_2$-), 3.0–3.3 (-SCH$_2$-), 3.6–3.8 (-NCH$_2$-), 3.8–4.0 (-NCH$_2$-), 4.3–4.5 (-OCH$_2$-), 4.5–4.7 (-COOCH$_2$-), 6.5–6.8 (ArH), 6.9–7.0 (ArH), 7.2–7.6 (ArH and C=CH), 7.8–8.1 ppm (ArH); ^{13}C NMR (150 MHz, CDCl$_3$, 298 K) δ = 22.86, 24.00, 47.44, 50.04, 51.44 55.44, 62.02, 122.14, 122.79, 123.14, 126.29, 128.73, 129.27, 129.82, 133.53, 138.65, 144.40, 146.45, 151.15, 156.34, 166.69 ppm; IR (KBr): $\tilde{\nu}$ = 1716 (C=O), 1316, 1130 cm^{-1} (-SO$_2$-); elemental analysis calcd (%) for $C_{864}H_{863}N_{181}O_{124}S_{30}$: C 62.03, H 5.20, N 15.16; found: C 61.06, H 5.87, N 14.75.

G5-S: According to the general procedure using compound **G2-8N$_3$-N** (6.91 mg, 0.00228 mmol) and **G2-≡-S** (80.0 mg, 0.0206 mmol). **G5-S** was obtained as orange powder (70.0 mg, 89.7 %). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ = 1.6–2.2 (-CH$_2$-), 2.7–2.9 (-CH$_2$C- and -CH$_2$-), 3.1–3.4 (-SCH$_2$-), 3.6–4.0 (-NCH$_2$-), 4.3–4.8 (-OCH$_2$- and -COOCH$_2$-), 6.4–6.8 (ArH), 6.9–7.0 (ArH), 7.2–7.6 (ArH and C=CH), 7.8–8.3 ppm (ArH); ^{13}C NMR (150 MHz, CDCl$_3$, 298 K): δ = 22.88, 24.01, 50.03, 55.46, 62.03, 112.14, 123.13, 126.29, 128.72, 129.27, 129.82, 133.52, 138.63, 144.37, 146.43, 151.15, 156.30, 166.68 ppm; IR (KBr): $\tilde{\nu}$ = 1716 (C=O), 1316, 1130 cm^{-1} (-SO$_2$-); elemental analysis calcd (%) for $C_{1760}H_{1759}N_{373}O_{252}S_{62}$: C 61.89, H 5.19, N 15.30; found: C 61.50, H 5.44, N 15.02.

Synthesis of core G0-3N$_3$: 1,3,5-Tris(bromomethyl)benzene (**S4**) (1.78 g, 5.0 mmol) and NaN$_3$ (1.95 g, 30.0 mmol) were dissolved in DMF (25 mL). The reaction was stirred for 12 h at 80 °C, then treated with H$_2$O and extracted with CHCl$_3$, 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 using petroleum ether/chloroform (1:2, v/v) as eluent to afford colorless oil **G0-3N$_3$** (1.17 g, 95.9 %). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ = 4.38 (s, 6 H, -CH$_2$-), 7.24 ppm (s, 3 H, -ArH-); ^{13}C NMR (75 MHz, CDCl$_3$, 298 K): δ = 53.89, 127.11, 136.62 ppm.

Synthesis of dendrimer G1-6Cl-S-GL: The procedure was similar to the synthesis of dendrimer **G1–4Cl-S**, but using chromophore **S4** (497.6 g, 1.1 mmol) and **G0-3N$_3$** (81.1 mg, 0.33 mmol). The crude product was purified by column chromatography using pure ethyl acetate as eluent to afford orange solid **G1-6Cl-S-GL** (447.9 mg, 84.0 %). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ = 2.12 (m, 6 H, -CH$_2$-), 2.83 (t, *J* = 6.0 Hz, 6 H, -CH$_2$C-), 3.19 (t, *J* = 6.0 Hz, 6 H, -SCH$_2$-), 3.71 (t, *J* = 6.0 Hz, 12 H, -NCH$_2$-), 3.85 (t, *J* = 6.0 Hz, 12 H, -CH$_2$Cl), 5.44 (s, 6 H, -NCH$_2$-), 6.79 (d, *J* = 8.7 Hz, 6 H, ArH), 7.09 (s, 3 H, C=CH), 7.31 (s, 3 H, ArH), 7.9–8.0 ppm (m, 18 H, ArH); ^{13}C NMR (75 MHz, CDCl$_3$, 298 K): δ = 22.21, 23.59, 40.07, 52.97, 55.02, 67.24, 107.53, 111.43, 121.48, 122.63, 125.77, 127.19, 128.76, 136.64, 138.42, 144.08, 146.16, 149.48, 155.64 ppm; IR (KBr): $\tilde{\nu}$ = 1316, 1131 cm^{-1} (-SO$_2$-); MALDI-TOF MS: *m/z* calcd for $C_{72}H_{78}Cl_6N_{18}O_6S_3$: 1623.4 $[M+Na]^+$; found: 1623.0.

Synthesis of dendrimer G1-6N$_3$-S-GL: The procedure was similar to the synthesis of dendrimer **G1-4N$_3$-S**, but using compound **G0-6Cl-S-GL** (360.0 mg, 0.225 mmol), NaN$_3$ (175.5 mg, 2.7 mmol). **G1-6N$_3$-S-GL** was obtained as orange solid (298.2 mg, 80.8 %). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ = 2.12 (s, br, 6 H, -CH$_2$-), 2.84 (s, br, 6 H, -CH$_2$C-), 3.20 (s, br, 6 H, -SCH$_2$-), 3.59 (s, br, 12 H, -CH$_2$Cl), 3.71 (s, br, 12 H, -NCH$_2$-), 5.43 (s, 6 H, -NCH$_2$-), 6.81 (d, *J* = 8.1 Hz, 6 H, ArH), 7.08 (s, 3 H, C=CH), 7.30 (s, 3 H, ArH), 7.9–8.0 ppm (m, 18 H, ArH); ^{13}C NMR (75 MHz, CDCl$_3$, 298 K): δ = 22.41, 23.81, 48.66, 50.59, 53.07, 55.22, 111.78, 121.46, 122.80, 125.92, 127.26, 128.94, 126.86, 138.56, 144.28, 146.43, 149.80, 155.94 ppm; IR (KBr): $\tilde{\nu}$ = 2097 (-N$_3$), 1316, 1131 cm^{-1} (-SO$_2$-); MALDI-TOF MS: *m/z* calcd for $C_{72}H_{78}N_{36}O_6S_3$: 1673 $[M]^+$; found: 1674.

Synthesis of dendrimer G1-S-GL: The procedure was similar to the synthesis of dendrimer **G1-S**, but using chromophore **G0-≡-S** (102.9 mg, 0.165 mmol) and **G0-3N$_3$** (12.2 mg, 0.050 mmol). The crude product was purified by column chromatography using pure ethyl acetate as eluent to afford orange solid **G1-S-GL** (98.2 mg, 92.9 %). ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ = 1.63 (s, br, -CH$_2$-), 2.15 (m, -CH$_2$-), 2.84 (t, *J* = 8.0 Hz, -CH$_2$C-), 3.20 (t, *J* = 8.0 Hz, -SCH$_2$-), 3.93 (m, -NCH$_2$-), 4.58 (t, *J* = 8.0 Hz, -COOCH$_2$-), 5.44 (s, -NCH$_2$-), 6.71 (d, *J* = 8.0 Hz, ArH), 7.02 (s, C=CH), 7.40 (m, ArH), 7.52 (m, ArH), 7.8–8.0 ppm (m, ArH); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K): δ = 13.73, 19.18, 22.54, 23.94, 30.57, 49.84, 53.21, 55.35, 61.81, 65.56, 112.00, 121.62, 112.00, 121.62, 122.90, 126.06, 127.41, 128.50, 128.84, 129.07, ‘19.63, 130.62, 136.21, 138.31, 145.84, 150/99, 166.46 ppm; IR (KBr): $\tilde{\nu}$ = 1711 (C=O), 1316, 1130 cm^{-1} (-SO$_2$-); MALDI-TOF MS: *m/z* calcd for $C_{114}H_{108}N_{18}O_{18}S_3$: 2135.7 $[M+Na]^+$; found: 2135.4; elemental analysis calcd (%) for $C_{114}H_{108}N_{18}O_{18}S_3$: C 64.76, H 5.15, N 11.92; found: C 64.22, H 4.99, N 12.21.

General procedure for the synthesis of G2-S-GL, G3-S-GL and G4-S-GL: A mixture of **G1-6N$_3$-S-GL** (1.00 equiv), different end-capped dendrons (7.00 equiv), and CuBr (3.00 equiv) were dissolved in DMF (0.02 M-N$_3$) under nitrogen in a Schlenk flask, then *N,N,N,N,N*-pentamethyldiethylenetriamine (PMDETA) (3.00 equiv) was added. After the mixture was stirred at 25–30 °C for 6 h, the reaction was terminated by addition of water. The precipitate was purified by repeating precipitations of their THF or $CHCl_3$ solutions into ethyl acetate or acetone, and then filtered and washed with lots of ethyl acetate or acetone, dried in vacuum at 40 °C to a constant weight.

G2-S-GL: According to the general procedure using compound **G1-6N_3-S-GL** (32.8 mg, 0.020 mmol) and **G0-≡-S** (87.3 mg, 0.14 mmol). **G2-Ph-GL** was obtained as orange powder (86.4 mg, 80.3 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): $\delta = 1.62$ (s, br, -CH_2-), 2.80 (s, br, -CH_2C-), 3.16 (s, br, -SCH_2-), 3.73 (s, br, -NCH_2-), 3.95 (s, br, -NCH_2-), 4.34 (s, br, -NCH_2-), 4.58 (s, br, -COOCH_2-), 5.40 (s, -NCH_2-), 6.72 (s, br, ArH), 6.97 (d, $J = 8.7$ Hz, ArH), 7.05 (s, C=CH), 7.42 (s, br, ArH), 7.56 (s, br, ArH), 7.8–8.1 ppm (m, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): $\delta = 22.60$, 23.71, 29.61, 47.16, 49.77, 51.23, 53.09, 55.18, 61.71, 111.88, 121.53, 122.41, 122.84, 125.99, 127.25, 128.43, 129.00, 129.54, 133.24, 138.42, 144.17, 144.58, 146.21, 149.13, 150.85, 156.09, 166.39 ppm; IR (KBr): $\tilde{\nu} = 1710$ (C=O), 1316, 1131 cm^{-1} (-SO_2-); MALDI-TOF MS: m/z calcd for $C_{282}H_{276}N_{54}O_{42}S_9$: 5405 $[M+Na]^+$; found: 5406; elemental analysis calcd for $C_{282}H_{276}N_{54}O_{42}S_9$: C 62.93, H 5.17, N 14.05; found: C 62.54, H 5.23, N 14.37.

G3-S-GL: According to the general procedure using compound **G1-6N_3-S-GL** (16.4 mg, 0.010 mmol) and **G1-≡-S** (113.1 mg, 0.066 mmol). **G3-Ph-GL** was obtained as orange powder (82.1 mg, 68.9 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): $\delta = 1.6$–2.4 (-CH_2-), 2.76 (s, br, -CH_2C-), 3.14 (s, br, -SCH_2-), 3.71 (s, br, -NCH_2-), 3.93 (s, br, -NCH_2-), 4.43 (s, br, -NCH_2-), 4.55 (s, br, -COOCH_2-), 5.33 (s, -NCH_2-), 6.69 (s, br, ArH), 6.96 (s, br, ArH), 7.2–7.6 (ArH and C=CH), 7.7–8.2 ppm (ArH); ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): $\delta = 22.86$, 24.01, 50.06, 55.46, 62.02, 112.15, 123.14, 126.30, 128.73, 129.28, 129.84, 133.54, 138.67, 144.42, 146.38, 151.15, 156.34, 166.69 ppm; IR (KBr): $\tilde{\nu} = 1711$ (C=O), 1316, 1131 cm^{-1} (-SO_2-); MALDI-TOF MS: m/z calcd for $C_{618}H_{612}N_{126}O_{90}S_{21}$: 11 954 $[M+Na]^+$; found: 11 941; elemental analysis calcd (%) for $C_{618}H_{612}N_{126}O_{90}S_{21}$: C 62.28, H 5.18, N 14.81; found: C 62.77, H 5.29, N 14.44.

G4-S-GL: According to the general procedure using compound **G1-6N_3-S-GL** (5.1 mg, 0.0032 mmol) and **G2-≡-S** (80.0 mg, 0.0206 mmol). **G4-Ph-GL** was obtained as orange powder (65.7 mg, 84.4 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): $\delta = 1.68$ (s, br, -CH_2-), 2.74 (s, br, -CH_2C-), 3.13 (s, br, -SCH_2-), 3.70 (s, br, -NCH_2-), 3.91 (s, br, -NCH_2-), 4.42 (s, br, -NCH_2-), 4.54 (s, br, -COOCH_2-), 5.35 (s, -NCH_2-), 6.79 (s, br, ArH), 6.94 (s, br, ArH), 7.2–7.6 (ArH and C=CH), 7.7–8.1 ppm (ArH); ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): $\delta = 22.87$, 24.02, 29.93, 47.46, 50.08, 55.49, 62.02, 112.20, 123.12, 126.26, 128.71, 129.26, 129.82, 133.50, 138.79, 144.47, 146.44, 151.21, 156.35, 166.65 ppm; IR (KBr): $\tilde{\nu} = 1710$ (C=O), 1316, 1131 cm^{-1} (-SO_2-); elemental analysis calcd (%) for $C_{1290}H_{1284}N_{270}O_{186}S_{45}$: C 62.00, H 5.18, N 15.13; found: C 62.93, H 5.53, N 15.44.

Preparation of polymer thin-films: The dendrimers were dissolved in THF (concentration ≈3 wt %), and the solutions were filtered through syringe filters. The dendrimer films were spin coated onto indium-tin-oxide (ITO)-coated glass substrates, which were cleaned by DMF, acetone, distilled water, and THF sequentially in an ultrasonic bath before use. Residual solvent was removed by heating the films in a vacuum oven at 40 °C.

NLO measurement of poled films: The second-order optical nonlinearity of the polymers was determined by in situ second harmonic generation (SHG) experiment using a closed temperature-controlled oven with optical windows and three needle electrodes.[15] The films were kept at 45° to the incident beam and poled inside the oven, and the SHG intensity was monitored simultaneously. Poling conditions were as follows: temperature, different for each polymer (Table 4); voltage, 7.8 kV at the needle point; gap distance, 0.8 cm. The SHG measurements were carried out with an Nd:YAG laser operating at a 10 Hz repetition rate and an 8 ns pulse width at 1064 nm. A Y-cut quartz crystal served as the reference.

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[1] a) D. M. Burland, R. D. Miller, C. A. Walsh, *Chem. Rev.* **1994**, *94*, 31–75; b) Y. Bai, N. Song, J. P. Gao, X. Sun, X. Wang, G. Yu, Z. Y. Wang, *J. Am. Chem. Soc.* **2005**, *127*, 2060–2621; c) T. J. Marks, M. A. Ratner, *Angew. Chem.* **1995**, *107*, 167–187; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 155–173; d) D. Yu, A. Gharavi, L. P. Yu, *J. Am. Chem. Soc.* **1995**, *117*, 11680–11686; e) S. R. Marder, B. Kippelen, A. K. Y. Jen, N. Peyghambarian, *Nature* **1997**, *388*, 845–851; f) M. Lee, H. E. Katz, C. Erben, D. M. Gill, P. Gopalan, J. D. Heber, D. J. McGee, *Science* **2002**, *298*, 1401–1403; g) Y. Shi, C. Zhang, H. Zhang, J. H. Bechtel, L. R. Dalton, B. H. Robinson, W. H. Steier, L. R. Dalton, *Science* **2000**, *288*, 119–122; h) C. V. Mclaughlin, M. Hayden, B. Polishak, S. Huang, J. D. Luo, T.-D. Kim, A. K. Y. Jen, *Appl. Phys. Lett.* **2008**, *92*, 151107; i) L. R. Dalton, P. A. Sullivan, D. H. Bale, *Chem. Rev.* **2010**, *110*, 25–55; j) J. D. Luo, X. H. Zhou, A. K. Y. Jen, *J. Mater. Chem.* **2009**, *19*, 7410–7424; k) J. D. Luo, S. Huang, Z. W. Shi, B. M. Polishak, X. H. Zhou, A. K. Y. Jen, *Chem. Mater.* **2011**, *23*, 544–553.

[2] a) S.-H. Jang, J. Luo, N. M. Tucker, A. Leclercq, E. Zojer, M. A. Haller, T.-D. Kim, J.-W. Kang, K. Firestone, D. Bale, D. Lao, J. B. Benedict, D. Cohen, W. Kaminsky, B. Kahr, J.-L. Bredas, P. Reid, L. R. Dalton, A. K.-Y. Jen, *Chem. Mater.* **2006**, *18*, 2982–2988; b) S. R. Marder, L. T. Cheng, B. G. Tiemann, A. C. Friedli, M. Blanchard-Desce, J. W. Perry, J. Skindhøj, *Science* **1994**, *263*, 511–514; c) Q. Li, Z. Li, F. Zeng, W. Gong, Z. Li, Z. Zhu, Q. Zeng, S. Yu, C. Ye, J. Qin, *J. Phys. Chem. B* **2007**, *111*, 508–514; d) B. H. Robinson, L. R. Dalton, *J. Phys. Chem. A* **2000**, *104*, 4785–4795; e) B. H. Robinson, L. R. Dalton, H. W. Harper, A. Ren, F. Wang, C. Zhang, G. Todorova, M. Lee, R. Aniszfeld, S. Garner, A. Chen, W. H. Steier, S. Houbrecht, A. Persoons, I. Ledoux, J. Zyss, A. K.-Y. Jen, *Chem. Phys.* **1999**, *245*, 35–50.

[3] L. R. Dalton, W. H. Steier, B. H. Robinson, C. Zhang, A. Ren, S. Garner, A. Chen, T. Londergan, L. Irwin, B. Carlson, L. Fifield, G. Phelan, C. Kincaid, J. Amend, A. K.-Y. Jen, *J. Mater. Chem.* **1999**, *9*, 1905–1920.

[4] a) M. J. Cho, D. H. Choia, P. A. Sullivan, A. J.-P. Akelaitis, L. R. Dalton, *Prog. Polym. Sci.* **2008**, *33*, 1013–1058; b) Y. V. Pereverzev, K. N. Gunnerson, O. V. Prezhdo, P. A. Sullivan, Y. Liao, B. C. Olbricht, A. J. P. Akelaitis, A. K.-Y. Jen, L. R. Dalton, *J. Phys. Chem. C* **2008**, *112*, 4355–4363.

[5] a) H. Ma, S. Liu, J. Luo, S. Suresh, L. Liu, S. H. Kang, M. Haller, T. Sassa, L. R. Dalton, A. K. Y. Jen, *Adv. Funct. Mater.* **2002**, *12*, 565–574; b) W. Shi, J. Luo, S. Huang, X.-H. Zhou, T.-D. Kim, Y.-J. Cheng, B. M. Polishak, T. R. Younkin, B. A. Block, A. K.-Y. Jen, *Chem. Mater.* **2008**, *20*, 6372–6377.

[6] a) Z. Li, Z. Li, C. Di, Z. Zhu, Q. Li, Q. Zeng, K. Zhang, Y. Liu, C. Ye, J. Qin, *Macromolecules* **2006**, *39*, 6951–6961; b) Q. Zeng, Z. Li, Z. Li, C. Ye, J. Qin, B. Z. Tang, *Macromolecules* **2007**, *40*, 5634–5637; c) Q. Li, Z. Li, C. Ye, J. Qin, *J. Phys. Chem. B* **2008**, *112*, 4928–4933; d) Z. Li, P. Li, S. Dong, Z. Zhu, Q. Li, Q. Zeng, Z. Li, C. Ye, J. Qin, *Polymer* **2007**, *48*, 3650–3657; e) Z. Li, S. Dong, G. Yu, Z. Li, Y. Liu, C. Ye, J. Qin, *Polymer* **2007**, *48*, 5520–5529; f) Z. Li, S. Dong, P. Li, Z. Li, C. Ye, J. Qin, *J. Polym. Sci. Part A* **2008**, *46*, 2983–2993; g) Z. Li, Q. Li, J. Qin, *Polym. Chem.* **2011**, *2*, 2723–2740; h) Z. Li, G. Qiu, C. Ye, J. Qin, Z. Li, *Dyes Pigm.* **2012**, *94*, 16–22; i) Q. Li, C. Lu, J. Zhu, E. Fu, C. Zhong, S. Li, Y. Cui, J. Qin, Z. Li, *J. Phys. Chem. B* **2008**, *112*, 4545–4551; j) Z. Li, Z. Qi, G. Yu, Z. Li, C. Ye, Y. Liu, J. Qin, *Macromol. Rapid Commun.* **2008**, *29*, 136–141; k) Z. Li, Q. Zeng, Z. Li, S. Dong, Z. Zhu, Q. Li, C. Ye, C. Di, Y. Liu, J. Qin, *Macromolecules* **2006**, *39*, 8544–8546.

[7] a) W. Wu, C. Ye, G. Yu, Y. Liu, J. Qin, Z. Li, *Chem. Eur. J.* **2012**, *18*, 4426–4434; b) W. Wu, C. Li, G. Yu, Y. Liu, C. Ye, J. Qin, Z. Li, *Chem. Eur. J.* **2012**, *18*, 11019–11028; c) W. Wu, L. Huang, L. Xiao,

Q. Huang, R. Tang, C. Ye, J. Qin, Z. Li, *RSC Adv.* **2012**, *2*, 6520–6526; d) W. Wu, Q. Huang, G, Qiu, J. Qin, Z. Li, *J. Mater. Chem.* **2012**, *22*, 18486–18495; e) Z. Li, W. Wu, C. Ye, J. Qin, Z. Li, *Polymer* **2012**, *53*, 153–160.

[8] a) Z. Li, G. Yu, W. Wu, Y. Liu, C. Ye, J. Qin, Z. Li, *Macromolecules* **2009**, *42*, 3864–3868; b) Z. Li, W. Wu, Q. Li, G. Yu, L. Xiao, Y. Liu, C. Ye, J. Qin, Z. Li, *Angew. Chem.* **2010**, *122*, 2823–2827; *Angew. Chem. Int. Ed.* **2010**, *49*, 2763–2767; c) W. Wu, L. Huang, C. Song, G. Yu, C. Ye, Y. Liu, J. Qin, Q. Li, Z. Li, *Chem. Sci.* **2012**, *3*, 1256–1261.

[9] P. A. Sullivan, H. Rommel, Y. Liao, B. C. Olbricht, A. J. P. Akelaitis, K. A. Firestone, J.-W. Kang, J. Luo, J. A. Davies, D. H. Choi, B. E. Eichinger, P. J. Reid, A. Chen, A. K. Y. Jen, B. H. Robinson, L. R. Dalton, *J. Am. Chem. Soc.* **2007**, *129*, 7523–7530.

[10] a) Z. Li, G. Yu, P. Hu, C. Ye, Y. Liu, J. Qin, Z. Li, *Macromolecules* **2009**, *42*, 1589–1596; b) Z. Li, W. Wu, G. Qiu, G. Yu, Y. Liu, C. Ye, J. Qin, Z. Li, *J. Polym. Sci. Part A* **2011**, *49*, 1977–1987; c) W. Wu, Y. Fu, C. Wang, C. Ye, J. Qin, Z. Li, *Chem. Asian J.* **2011**, *6*, 2787–2795.

[11] a) Y. Zhang, R. Burzynski, S. Ghosal, M. K. Casstecens, *Adv. Mater.* **1996**, *8*, 111–125, and references therein; b) F. Wang, A. W. Harper, M. S. Lee, L. R. Dalton, *Chem. Mater.* **1999**, *11*, 2285–2288; c) B. Cho, S. Lee, K. Son, Y. Kim, J. Doo, G. Lee, T. Kang, S. Jeon, *Chem. Mater.* **2001**, *13*, 1438–1440; d) L. R. Dalton, *Adv. Polym. Sci.* **2002**, *158*, 1–82; e) J. Zyss, I. Ledoux, *Chem. Rev.* **1994**, *94*, 77–105.

[12] A. Ulman, C. S. Willand, W. Kohler, D. R. Robello, D. J. Williams, L. Handley, *J. Am. Chem. Soc.* **1990**, *112*, 7083–7090.

[13] a) Z. Muchtar, M. Schappacher, A. Deffieux, *Macromolecules* **2001**, *34*, 7595–7600; b) M. W. Weimer, J. M. J. Fréchet, I. Gitsov, *J. Polym. Sci. Part A* **1998**, *36*, 955–970; c) Y. Kim, O. W. Webster, *Macromolecules* **1992**, *25*, 5561–5572.

[14] M. Kauranen, T. Verbiest, C. Boutton, M. N. Teeren, K. Clays, A. J. Schouten, R. J. M. Nolte, A. Persoons, *Science* **1995**, *270*, 966–969.

[15] a) Z. Li, J. Qin, S. Li, C. Ye, J. Luo, Y. Cao, *Macromolecules* **2002**, *35*, 9232–9235; b) Z. Li, C. Huang, J. Hua, J. Qin, Z. Yang, C. Ye, *Macromolecules* **2004**, *37*, 371–376; c) Z. Li, A. Qin, J. W. Y. Lam, Y. Dong, C. Ye, I. D. Williams, B. Z. Tang, *Macromolecules* **2006**, *39*, 1436–1442; d) Z. Li, J. Qin, A. Qin, C. Ye, *Polymer* **2005**, *46*, 363–368; e) Z. Li, W. Gong, J. Qin, Z. Yang, C. Ye, *Polymer* **2005**, *46*, 4971–4978; f) Z. Li, J. Hua, Q. Li, C. Huang, A. Qin, C. Ye, J. Qin, *Polymer*, **2005**, *46*, 11940–11948.

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Dendrimers

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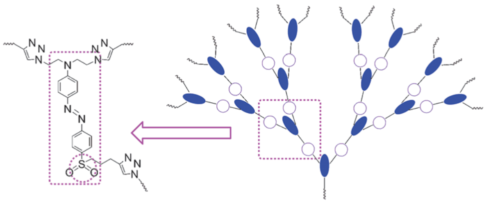
From Nitro- to Sulfonyl-Based Chromophores: Improvement of the Comprehensive Performance of Nonlinear Optical Dendrimers



Branching out: Through the combination of a divergent and convergent approach, by using the powerful "click-chemistry" reaction, two new series of sulfonyl-chromophore-based high-generation nonlinear optical (NLO) dendrimers were conveniently prepared in satisfactory yields (see figure). These dendrimers exhibited large second harmonic generation coefficient (d_{33}) values, as well as outstanding optical transparencies and NLO stabilities, simultaneously.