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### Using Two Simple Methods of Ar-Ar<sup>F</sup> Self-Assembly and Isolation Chromophores to Further Improve the Comprehensive Performance of NLO Dendrimers\*\*

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Abstract: Herein, through a combination of divergent and convergent approaches, coupled with the utilization of the powerful Sharpless "click chemistry" reaction, two series of high-generation nonlinear optical (NLO) dendrimers have been conveniently prepared in high purity and satisfactory yields. Perfluoroaromatic rings and isolation chromophores were introduced to further improve their comprehensive performance. Thanks to the effects of  $Ar-Ar^{F}$  self-assembly and the isolation chromophores, coupled with perfect 3D spatial isolation from the highly

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**G5-PFPh-NS** displayed very large NLO efficiency (up to  $257 \text{ pm V}^{-1}$ ), which is, to the best of our knowledge, the new record highest value reported so far for simple azo chromophore moieties. High-quality wide optical transparency and good stability were also achieved.

branched structure of the dendrimer,

### Introduction

Over the past decade, a great deal of effort has been devoted to the search for-and preparation of-organic/polymeric nonlinear optical (NLO) materials because of their promise as candidates for future technological applications, such as frequency doublers, optical-storage devices, and electrooptic (EO) switches and modulators.<sup>[1]</sup> Large optical nonlinearity, low optical loss, and excellent temporal stability of the dipole orientation are important challenges that scientists face in designing second-order NLO materials.<sup>[2,3]</sup> Of these, the efficient translation of the large  $\beta$  values of the organic chromophores into high macroscopic NLO activities of the polymers is the major problem, because the strong dipole-dipole interactions between the chromophore moieties with a donor- $\pi$ -acceptor (D- $\pi$ -A) structure would make the pole-induced noncentrosymmetric alignment of chromophore moieties (which is necessary for the materials to exhibit a NLO effect) a daunting task during the poling process under an electric field.<sup>[3]</sup> Fortunately, according to the experimental results and theoretical analysis of Jen, Dalton, and co-workers, the site-isolation principle (control

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[\*\*] NLO: nonlinear optical.

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duction of isolation groups) was considered to be an efficient approach for minimizing these interactions and enhancing the poling efficiency.<sup>[3a,4]</sup> Based on this principle, various structures of chromophores and other materials have been developed, from linear to various other shapes, such as L-shaped, X-shaped, H-shaped, star-shaped, and so on, to improve their topological structures.<sup>[5]</sup> Among these topologies, dendritic NLO materials, including hyperbranched polymers, dendronized polymers, and dendrimers, have been considered to be a very promising molecular topology for the next generation of highly efficient NLO materials, owing to their special 3D global highly branched structure (Figure 1).<sup>[6,7]</sup>

the shape of a spherical-shaped chromophore by the intro-

Recently, based on the excellent work mentioned above, as well as our previous conclusions on "the concept of a suitable isolation group",<sup>[8]</sup> we designed and synthesized a series of NLO dendrimers, **G1–G5** (see the Supporting Information, Schemes S1–S3),<sup>[9]</sup> that demonstrated excellent NLO activities (the  $d_{33}$  value of **G5** was up to 193.1 pm V<sup>-1</sup>, which was the highest value for simple azo chromophore moieties at that time). On increasing the loading density of the chromophore moieties, the tested NLO effects also increased, which indicated that the frequently observed asymptotic dependence of EO activity on the density of chromophore loading may be overcome through rational design, in accordance with the predictions of Sullivan, Robinson, Dalton, and co-workers.<sup>[10]</sup>

However, was that the limit of NLO dendrimers and could the NLO performance of dendrimers be enhanced further? Thus, additional research is still needed. For chemists, the general approach for improving the performance of materials is to modify their chemical structures on the molecular level. In most of the previous cases, based on the site-iso-



Figure 1. Our original design concepts for the NLO dendrimers.

lation principle, the isolation groups that were used were non-polar and could only adjust the shape of the chromophore.<sup>[3-9]</sup> In fact, the interactions between two isolation groups and between a chromophore and an isolation group should also be considered when designing NLO materials. Very recently, two new ways to use these interactions to improve the performance of NLO materials have been reported: The first is the use of the aromatic/perfluoroaromatic (Ar-Ar<sup>F</sup>) self-assembly effect (see the Supporting Information, Charts S1 and S2) between two isolation groups, as proposed by Jen and co-workers (this method was also very recently confirmed by ourselves);<sup>[11]</sup> the second is the introduction of isolation chromophores (see the Supporting Information, Chart S3), as reported by ourselves in 2012.<sup>[12]</sup> However, reports on the application of these two methods in the synthesis of high-generation dendrimers are scarce.<sup>[12b]</sup>

On the other hand, it is known that the preparation of high-generation dendrimers is typically tedious and expensive because of the need for repetitive protection, deprotection, and purification steps. Thus, it would be unwise to modify the chemical structures of dendrimers directly without having any preliminary experience. Herein, we use hyperbranched polymers, which have similar topological structures to dendrimers but are much easier to prepare,<sup>[13]</sup> as model compounds. First, we designed and synthesized a series of azo-chromophore-containing AB<sub>2</sub>-type hyperbranched polytriazoles (PS1-PS4; see the Supporting Information, Chart S4) that contained perfluoroaromatic rings in different parts of these hyperbranched polymers.<sup>[14]</sup> The use of pentafluorophenyl groups on the periphery produced higher  $d_{33}$  values than "normal" phenyl groups in the same positions, whereas the use of perfluoroaromatic rings in the interior architecture produced slightly lower  $d_{33}$  values (see the Supporting Information, Table S1). Inspired by this result, we designed and synthesized a new series of NLO dendrimers, G1-PFPh-N-G5-PFPh-N (Figure 2; PFPh indicates that their end-capped groups are pentafluorophenyl moieties to differentiate them from dendrimers G1-G5 that we reported previously, and N indicates that these dendrimers consist of a nitro-based chromophore). The  $d_{33}$  value of **G5-PFPh-N** was determined to be  $206 \text{ pm V}^{-1}$ , which was higher than that of G5. Also, isolation chromophores should be introduced into dendrimers to further improve their NLO activities. Model hyperbranched polymers PS5 and PS6 (see the Supporting Information, Chart S5) were synthesized from an AB4-type monomer that contained two chromophores with regular structures.<sup>[12a]</sup> The results showed that placing the main chromophores at the periphery would enhance its  $d_{33}$  value to a large degree, whereas the NLO coefficient of the hyperbranched polymers that contained isolation chromophores at the periphery exhibited almost no improvement (see the Supporting Information, Table S1). Thus, dendrimers G2-PFPh-NS-G5-PFPh-NS (Figure 2; NS indicates that the nitro- and sulfonyl-based chromophores are regular arranged, to differentiate them from dendrimers G1-PFPh-N-G5-PFPh-N), which had nitro-based azo chromophores at their periphery, were also prepared. Excitingly, the  $d_{33}$  value of G5-PFPh-NS was determined to be  $257 \text{ pm V}^{-1}$ , which is the new record highest value reported so far for simple azo chromophore moieties. Herein, we report the syntheses, characterization, and properties of these new dendrimers in detail.

### **Results and Discussion**

**Synthesis:** In general, dendrimers can be constructed through divergent (a growing pattern from a multivalent core) or convergent synthetic strategies (a dendron is grafted onto the core).<sup>[15,16]</sup> However, these tedious, multistep synthetic procedures often make the preparation of dendrimers relatively costly and they often encounter several difficulties, such as incomplete reaction of the end-groups in the divergent approach and steric hindrance between the reactive segments and the core molecule in the convergent strategy.<sup>[16a]</sup> Fortunately, through a combination of both divergent and convergent approaches (a "double-stage" method),<sup>[7b,17]</sup> as proposed by Fréchet and co-workers,<sup>[17a]</sup> the syn-



Figure 2. Structures of three series of dendrimers (G3 as examples) and their NLO coefficients.

cates there was a terminal alkyne group in this dendrimer) could be easily prepared, without the need for protection/deprotection steps. However, this approach was only appropriate for the preparation of low-generation dendrimers because of the large steric effects and the difficulty of chromatographic separation. For example, in the synthesis of G2-=-PFPh-N, the yield was not higher than 57.3%, even though the azocoupling reaction was conducted over 5 days, whereas the yield of G1-≡-PFPh-N was 79.6%. Thus, the yields of G3-**≡-PFPh-N** and **G4-≡-PFPh-N** in the subsequent steps would be much lower. On the other hand, the core compound (G2- $8N_3-N$ ,  $-8N_3$  indicates there were eight azide groups on the periphery of this dendrimer) was synthesized through a divergent approach from an AB<sub>2</sub>type monomer (Scheme 2). As with the convergent approach, this route was also not appropriate for the preparation of high-generation dendrimers, because the end-groups did not react completely, thus leading to structural defects. However, G5-PFPh-N could be obtained route 3 (Figure 3), through which is a combination of both divergent and convergent approaches, from the click reaction between G2-8N<sub>3</sub>-N and G2-≡-PFPh-N. Thus, by using this "double-stage" approach, the number of required synthetic steps for the preparation of dendrimers high-generation could be decreased to a large degree. Meanwhile, the purification of G3-PFPh-N, G4-PFPh-N, and G5-PFPh-N was

thetic efficiency could be rapidly raised. Thus, this well-designed "double-stage" approach was also used herein to synthesize NLO dendrimers (Figure 3).

Schemes 1–3 show our synthetic routes to **G5-PFPh-N**. In a convergent approach (Scheme 1), by taking advantage of a combination of click chemistry<sup>[18]</sup> and azo-coupling reac-

very easy, through repeated precipitation of solutions in THF with EtOAc, by taking advantage of the different solubilities of the product and the reactant (Scheme 3). On the contrary, if we used a "one-stage" approach, the purification of high-generation dendrimers would be highly problematic. Actually, even with this "double-stage" approach, there

tions, G2- $\equiv$ -PFPh-N ( $\equiv$  indi-

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Figure 3. Different approaches for the synthesis of the NLO dendrimers used here.

were still different possible routes for the synthesis of highgeneration dendrimers (Table 1). For example, **G4-PFPh-N** would be the product of "click" reactions between **G2-8N<sub>3</sub>-**

Table 1. Different synthetic routes to dendrimers G3-PFPh-N, G4-PFPh-N, and G5-PFPh-N.

	Compound 1	G1-4N <sub>3</sub> -N	G2-8N <sub>3</sub> -N		
G0-≡-PFPh-N			G3-PFPh-N <sup>[a]</sup>		
G1-≡-PFPh-N		G3-PFPh-N	G4-PFPh-N <sup>[a]</sup>		
G2-≡-PFPh-N	G3-PFPh-N	G4-PFPh-N	G5-PFPh-N <sup>[a]</sup>		

[a] These routes were used herein.

N and G1= $\equiv$ -PFPh-N or between G1-4N<sub>3</sub>-N and G2= $\equiv$ -PFPh-N. Herein, the first route was used because of the large difference in molecular weight between the end-capped dendron (G1= $\equiv$ -PFPh-N) and the product (G4-PFPh-N), which would afford easy purification. For the same reason, the other high-generation dendrimers were prepared through their chosen synthetic routes.

The synthetic route to dendrimers **G2-PFPh-NS–G5-PFPh-NS**, in which two different chromophores (the sulfonyl- and nitro-based ones) are arranged in an orderly manner, should be similar to that to **G1-PFPh-N–G5-PFPh-N**, which only contain one type of chromophore; the synthetic route is shown in the Supporting Information, Schemes S4–S6 and Table S2.

Characterization and self-assembly effect: These newly prepared dendrimers were well-characterized by spectroscopic methods (for detailed results, see the Supporting Information). Their FTIR spectra showed absorption bands that were associated with the nitro groups at about 1515 and 1338 cm<sup>-1</sup>, as well as a band that was associated with both nitro and sulfonyl groups (1140 cm<sup>-1</sup>), thus indicating the successful introduction of the chromophore moieties into the dendrimers (see the Supporting Information, Figures S1 and S2). Also, the peak for the azido groups (at about 2100 cm<sup>-1</sup>) in the azido-containing core disappeared in the spectra of high-generation dendrimers, whereas an absorption at 1740 cm<sup>-1</sup>, which came from the carbonyl groups in the end-capped chromophores, appeared. These results showed that the target dendrimers were successfully prepared from the click chemistry reaction by using this "double-stage" approach. This conclusion was also confirmed by NMR spectroscopy. For example, in all of the <sup>1</sup>H NMR spectra of the high-generation dendrimers, some characteristic peaks of the chromophores and of the COOCH<sub>2</sub> protons (about  $\delta = 4.6$  ppm) in the end-capped groups were observed, whilst the peak at about  $\delta = 3.6$  ppm,



Scheme 1. Synthesis of end-capped dendrons G1-=-PFPh-N and G2-=-PFPh-N

which was assigned to the protons in the  $CH_2N_3$  group, disappeared.

Analysis of the dendritic growth by MS (MALDI-TOF) and by GPC (see the Supporting Information, Table S3) was performed after each step, as shown in Schemes 1–3 and the Supporting Information, Schemes S4–S6. MS (MALDI-TOF) is a good method to confirm the exact molecular weight of dendrimers; the mass spectra of the prepared dendrimers are shown in the Supporting Information, Figures S29–S35, and all of the experimental results are in good agreement with the expected molecular weights of the structures. However, unfortunately, we failed to detect any signals within the appropriate mass range for high-generation dendrimers (when the generation number was higher than 3); one possible reason for this result might be that their larger molecular weight resulted in much-lower peak intensity. Thus, GPC measurements were conducted and the results are summarized in the Supporting Table S3. Information, The trends in GPC results were consistent with the actual molecular weights: with each increase in the generation number of the dendrimers, the  $M_{\rm w}$  values also increased with low PDIs. Herein, a very interesting phenomenon was observed. As we know, GPC analysis by using linear polystyrenes as calibration standards often underestimates the molecular weight of dendrimers with 3D branched structures because of their quite different hydrodynamic radii.<sup>[19]</sup> On the contrary, if the difference between the tested value and the true one were higher, its hydrodynamic radius should be more different from that of linear polymers and its topological structure might be closer to spherical. Herein, on increasing the generation number of the dendrimers, the globular shape improved and the difference between the measured and calculated values also increased (Figure 4). In addition, the difference increased on the introduction of perfluoroaromatic rings (Figure 4). This indicates

that the topological structure became closer to ideal after the perfluoroaromatic rings were introduced, especially in high-generation dendrimers, possibly owing to an Ar–Ar<sup>F</sup> self-assembly effect. Moreover, compared with **Gn-PFPh-N**, **Gn-PFPh-NS** showed larger differences (Figure 4), which indicated that **Gn-PFPh-NS** had a more perfect topological structure. In our previous work, our experimental results showed that NLO activity would only increase in polymers with a regular AB structure (see the Supporting Information, Chart S3, **P4**), that is, the isolation chromophore might be next to the main chromophore.<sup>[12]</sup> Herein, the GPC re-



Scheme 2. Synthesis of the dendrimer core, G2-8N<sub>3</sub>-N.

sults led us to a preliminary conclusion: The interactions between isolation chromophores and main chromophores would improve the topological structure of the polymers or dendrimers, which would further affect their poling behavior.

To further confirm the GPC results, <sup>19</sup>F NMR spectroscopy of all of the dendrimers was performed. From the chemical structure of these dendrimers, three types of F atoms were distinguished for the pentafluorophenyl groups; correspondingly, in their <sup>19</sup>F NMR spectra, there should only be three kinds of peaks. However, if an Ar–Ar<sup>F</sup> self-assembly effect was operative in these dendrimers, some additional peaks would be observed. The results were encouraging (Figure 5): if the generation number was higher than three, several new peaks appeared in addition to the original peaks for the pentafluorophenyl groups, which was consistent with the GPC results that the higher the generation number, the stronger the  $Ar-Ar^F$  self-assembly effect. However, this result did not confirm that there was no self-assembly effect in the lower-generation dendrimers; perhaps, the self-assembly effect was just a little too weak to be observed by <sup>19</sup>F NMR spectroscopy.

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In our previous analysis of dendrimers G1-G5, an increase in generation number led to better site-isolation effects and wider optical-transparency windows, which might have been due to the better 3D topological structure of high-generation dendrimers than low-generation dendrimers.<sup>[9]</sup> Presumably, the exterior benzene moieties and the interior triazole rings that surrounded the azo chromophore moieties also played a key role in shielding the chromophores from the solvatochromic effect. Herein, we confirmed that the Ar-Ar<sup>F</sup> self-assembly effect should make the topological structure of the dendrimers even better. Thus, we wondered whether the pentafluorophenyl groups at the periphery of these dendrimers would have an effect on their transparency. To answer this question, their UV/Vis spectra were recorded (see the Supporting Information, Fig-

ures S36–S47 and Table S4). As expected, in the solid films, the dendrimers that contained perfluoroaromatic rings exhibited blue-shifted absorption maxima compared with the dendrimers that only contained normal phenyl groups in our previous work (Figure 6), which demonstrated that the more perfect 3D topological structure could directly impede the strong intermolecular dipole–dipole interactions between the chromophore moieties and greatly contribute to the ordered noncentrosymmetric alignment during the poling process. Furthermore, owing to the presence of the sulfonyl chromophore, all of the maximum absorptions of the dendrimers that contained the isolation chromophore were blue-shifted even further compared with those that only contained one type of chromophore (Figure 6). Taking the highest-generation dendrimers in this work as an example

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Scheme 3. Synthesis of dendrimers G3-PFPh-N, G4-PFPh-N, and G5-PFPh-N.



Figure 4. Ratio between the measured and calculated molecular weights for different dendrimers;  $M_c$  is the calculated molecular weight and  $M_w$  is the measured value (determined by GPC).

(Figure 6B), the maximum absorption of compound **G5** was about 470 nm, which was already quite-largely blue-shifted compared to the low-generation dendrimers. Moreover, owing to its more ideal 3D topological structure, the maximum absorption of **G5-PFPh-N** was blue-shifted even further to 460 nm, whilst the maximum absorption of **G5-PFPh-NS** was only 443 nm. This blue-shifted absorption maximum of the dendrimers would result in wide opticaltransparency windows and contribute to practical applications in the field of photonics.

On the other hand, these dendrimers were thermally stable (see the Supporting Information, Figures S47 and S48); their temperatures for 5% weight loss are listed in Table 2 (higher than 230°C). Their degradation temperatures  $(T_d)$  were a little lower than those of dendrimers G1-G5, possibly owing to the presence of the not-so-stable pentafluorophenyl group. However, this result is already sufficient for NLO materials, because the temperature for their application in "real" systems could be below 200 °C. The glass-transition temperatures  $(T_{o})$  of the dendrimers were also investigated by using differential scanning calorimetry (DSC; Table 2). Similar to dendrimers G1-G5, the growth of the dendrimers also resulted in an increase in their  $T_{g}$ values and the  $T_{\rm g}$  values of the dendrimers that contained pentafluorophenyl groups were much higher than those that only contained phenyl groups (165°C for G5-PFPh-N versus 125°C for G5), which further confirmed that the Ar-Ar<sup>F</sup> self-assembly effect existed in these dendrimers. In addition, higher  $T_g$  values would improve the temporal stability of the dipole orientation of the chromophore in the dendrimers, which could contribute greatly to their practical application.

**NLO properties**: All of the NLO dendrimers exhibited good film-forming ability and their poled films were prepared for the evaluation of their NLO activity. A convenient technique to study their second-order NLO activity was to investigate the second-harmonic generation (SHG) processes, which are characterized by  $d_{33}$ , an SHG coefficient. The test

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Figure 5. <sup>19</sup>F NMR spectra of: A) dendrimers **G1-PFPh** to **N-G5-PFPh-N**, and B) dendrimers **G2-PFPh-NS** to **G5-PFPh-NS**.

Table 2. Physical and NLO data for the dendrimers.

Dendrimer	$T_{\rm g}^{[a]}$	$T_{d}^{[b]}$	$T_{\rm e}^{\rm [c]}$	$d_{33}^{[d]}$	$d_{33(\infty)}^{[e]}$	$arPsi^{[\mathrm{f}]}$	$N^{[g]}$
	[°C]	[°C]	[°C]	$[pm V^{-1}]$	$[\mathrm{pm}\mathrm{V}^{-1}]$		
G1-PFPh-N	59	252	85	84	15	0.12	0.326
G2-PFPh-N	78	243	105	89	16	0.16	0.411
G3-PFPh-N	103	237	125	108	21	0.22	0.444
G4-PFPh-N	135	236	125	187	38	0.28	0.459
G5-PFPh-N	165	233	135	206	42	0.34	0.466
G2-PFPh-NS	62	241	100	95	23	0.16	0.432
G3-PFPh-NS	119	233	125	109	26	0.26	0.464
G4-PFPh-NS	127	228	125	179	44	0.28	0.482
G5-PFPh-NS	142	241	140	257	65	0.39	0.488

[a] The glass-transition temperatures ( $T_g$ ) of the polymers were determined by DSC analysis under an argon atmosphere at a heating rate of 10°Cmin<sup>-1</sup>. [b] The temperatures of the polymers for 5% weight loss were determined by TGA analysis under a nitrogen atmosphere at a heating rate of 10°Cmin<sup>-1</sup>. [c] The optimal poling temperature. [d] Second harmonic generation (SHG) coefficient. [e] The non-resonant  $d_{33}$  values were calculated by using the approximate two-level model. [f] Order parameter  $\Phi = 1 - A_1/A_0$ , where  $A_1$  and  $A_0$  are the absorbance of the polymer film after and before corona poling, respectively. [g] Loading density of the effective chromophore moieties; this value contains both the main chromophore and the isolation chromophore.

procedure was similar to one that we had reported previously<sup>[8,9,12]</sup> and their  $d_{33}$  values were calculated from the experimental data at the 1064 nm fundamental wavelength (Table 2).



Figure 6. UV/Vis data of high-generation dendrimers: A) maximum absorption wavelengths of the dendrimers in thin films, and B) UV/Vis spectra of the dendrimers in thin films.

In our previous work, the  $d_{33}$  values increased from dendrimers **G1** (100.0 pm V<sup>-1</sup>) to **G5** (193.1 pm V<sup>-1</sup>), with an accompanying increasing in the loading density of the chromophore moieties; moreover, the more perfect the 3D structure of the dendrimers, the higher the  $d_{33}$  values.<sup>[9]</sup> Herein, a similar phenomenon appeared in the dendrimers that contained pentafluorophenyl groups: Changing the loading concentration of the chromophore moieties from 0.326 in **G1-PFPh-N** to 0.411 in **G2-PFPh-N**, 0.444 in **G3-PFPh-N**, 0.459 in **G4-PFPh-N**, and 0.466 in **G5-PFPh-N** led to an increase in the NLO coefficients from 84 in **G1-PFPh-N** to 89 in **G2-PFPh-N**, 108 in **G3-PFPh-N**, 187 in **G4-PFPh-N**, and 206 pm V<sup>-1</sup> in **G5-PFPh-N**. These encouraging results should

> be also ascribed to their more perfect 3D structures and to the isolation effect of the exterior pentafluorophenyl moieties and the interior triazole rings, which could decrease the strong electronic interactions between the chromophore moieties and enhance their poling efficiency, according to the "suitable isolation groups" concept; almost the same result was observed previously with dendrimers G1-G5. On the other hand, in comparison with dendrimer G5, which only contained normal phenyl groups at its periphery, G5-PFPh-N demonstrated a higher NLO coefficient (206 pm  $V^{-1}$ versus 193.1 pm  $V^{-1}$ ), which should be attributed to a strong Ar-Ar<sup>F</sup> self-assembly effect. However, in the low-generation dendrimers, pentafluorophenyl moieties made the  $d_{33}$  values lower, instead of higher as in the high-generation dendrimers. This result was understandable because it was wellknown that, in theory, under identical experimental conditions, the  $d_{33}$  value is proportional to the density of chromophore moieties. The use of pentafluorophenyl groups instead of normal phenyl moieties not only brought the self-assembly effect, but

also made the loading concentration of the chromophore moieties lower (Figure 7A, Table 2), because the atomic mass of the Fatom was much larger than that of the H atom. From their <sup>19</sup>F NMR spectra and GPC results, we

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Figure 7. A) Effective chromophore densities, and B)  $d_{33}$  values of different types of dendrimers; **Gn** (**■**), **Gn-PFPh-N** (**△**), **Gn-PFPh-NS** ( $\bigcirc$ ).

observed that the Ar–Ar<sup>F</sup> self-assembly effect in low-generation dendrimers was weak and that the improvement in their 3D topological structure from this effect could not compensate for the negative effects of the decreased chromophore-loading densities. Thus, the  $d_{33}$  values of **Gn**-**PFPh-N** in low-generation dendrimers were a little lower than those that only contained normal phenyl groups as the end-capped groups. On increasing the generation number, the Ar–Ar<sup>F</sup> self-assembly effect became stronger and the  $d_{33}$ values also increased (Figure 7B). As expected, the  $d_{33}$ value of **G4-PFPh-N** (187 pmV<sup>-1</sup>) was higher than that of **G4** (177 pmV<sup>-1</sup>) and the NLO coefficient of **G5-PFPh-N** was even as higher (206 pmV<sup>-1</sup>).

Based on dendrimers **G1-PFPh-N** to **G5-PFPh-N**, the structures of compounds **G2-PFPh-NS** to **G5-PFPh-NS** were further improved by the introduction of isolation chromophore moieties and this improvement could be reflected in their NLO coefficients: Almost all of the  $d_{33}$  values of **Gn-PFPh-NS** were higher than those of **Gn-PFPh-N** in the same generation (Figure 7B, Table 2). As an example, the  $d_{33}$  value of **G5-PFPh-NS** was as high as 257 pm V<sup>-1</sup>, which was more than 50 pm V<sup>-1</sup> higher than that of **G5-PFPh-N**. It is worth pointing out that this value is the new record highest value reported so far for simple azo chromophore moieties to the best of our knowledge.

Because the films of these dendrimers still showed some absorption at 532 nm (the doubled frequency of the 1064 nm fundamental wavelength), the NLO properties of the dendrimers should be smaller  $(d_{33(\infty)};$  Table 2), owing to the resonant-enhancement effect.<sup>[20]</sup> As mentioned above, the maximum absorption of these new dendrimers was blue-shifted compared to that of dendrimers G1-G5; thus, the increasing trend in the  $d_{33(\infty)}$  values of these dendrimers should be more obvious. In fact, the  $d_{33(\infty)}$  value of G5-PFPh-NS was  $65 \text{ pm V}^{-1}$ , which was almost twice that of dendrimer G5 (34  $\text{pm}\,\text{V}^{-1}$ ), thus making these dendrimers suitable for potential applications in the field of optics. This phenomenon also means that the introduction of pentafluorophenyl moieties or isolation chromophores into dendrimers (or polymers) is a new way of solving the contradictions between nonlinearity and transparency in some way.

To further explore the alignment of the chromophore moieties in these dendrimers, we measured their order parameter,  $\Phi$  (Table 2 and the Supporting Information, Figures S50–S58). According to the equation  $\Phi = 1 - A_1/A_0$ , the  $\Phi$  values of the dendrimers were calculated and the results are listed in Table 2. The trend in  $\Phi$  value was the same as that in the  $d_{33}$  values of the dendrimers, which further supported our conclusion.

De-poling experiments of the dendrimers were also conducted, in which the real-time decay of their SHG signals was monitored as the poled films were heated from 35 to 150 °C in air at a rate of 4 °Cmin<sup>-1</sup>. Figure 8 displays the



Figure 8. Decay curves of the SHG coefficients of the dendrimers as a function of temperature.

decay of the SHG coefficient of the dendrimers as a function of temperature. Owing to their high  $T_g$  values, which were derived from the Ar–Ar<sup>F</sup> effect, the temporal stability of the dipole orientation of these dendrimers was also improved. For **G5-PFPh-N**, the temperature for the decay was up to 111°C, which is promising for practical NLO applications.

#### Conclusion

In summary, by using a combination of divergent and convergent approaches, coupled with the powerful click-chemistry reaction, two new series of dendrimers were successfully obtained in which two new effects, that is, Ar-Ar<sup>F</sup> self-assembly and isolation chromophores, were used to further improve their comprehensive performance. These dendrimers exhibited very large  $d_{33}$  values (up to 257 pm V<sup>-1</sup>, which is the highest value reported so far for simple azo chromophore moieties), excellent optical transparency (the maximum absorption was only 443 nm in a film), and good stability. Thus, these successful examples might open up new avenues to synthesize more dendrimers with good NLO properties; moreover, we believe that, by modifying the polvmeric structure more intelligently, better performance could be achieved by utilizing these very simple azo chromophore moieties.

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## **FULL PAPER**

### **Experimental Section**

**Materials and instrumentation**: THF was dried over and distilled from a K-Na alloy under an atmosphere of dry nitrogen. DMF was dried over and distilled from CaH<sub>2</sub>. Compound 1, diazonium salts 2 and 3, G0= -PFPh-N, and dendronized cores G1-4N<sub>3</sub>-N, G2-8N<sub>3</sub>-N, G1-4N<sub>3</sub>-S, and G2-8N<sub>3</sub>-NS were prepared according to our previously reported procedures.<sup>[9,12a,b,14]</sup> *N,N,N,N*-pentamethyldiethylenetriamine (PMDETA) and pentafluorobenzoic acid were purchased from Alfa Aesar. All other reagents were used as received.

<sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were measured on Varian Mercury300, Varian Mercury600, or Bruker ARX400 spectrometers by using tetramethylsilane (TMS;  $\delta = 0$  ppm) as an internal standard. FTIR spectra were recorded on a PerkinElmer-2 spectrometer in the region 3000-400 cm<sup>-1</sup>. UV/Vis spectra were obtained on a Shimadzu UV-2550 spectrometer. MS (MALDI-TOF) was performed 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 micro-elemental analyzer. Gel-permeation chromatography (GPC) was used to determine the molecular weights 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 calibration standards, THF was used as an eluent, and the flow rate was 1.0 mLmin<sup>-1</sup>. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA449C thermal analyzer at a heating rate of 10°Cmin<sup>-1</sup> under a flow of nitrogen gas (flow rate: 50 cm<sup>3</sup>min<sup>-1</sup>). The thermal transitions of the polymers were investigated by using a METTLER differential scanning calorimeter DSC822e under a nitrogen atmosphere at a scanning rate of 10°Cmin<sup>-1</sup>. The melting points were uncorrected. The thickness of the films was measured on an Ambios Technology XP-2 profilometer.

Synthesis of dendrimer G1-PFPh-N: Chromophore G0-≡-PFPh-N (1.60 g, 2.0 mmol), N,N-bis(2-azidoethyl)aniline (1; 208 mg, 0.9 mmol),  $CuSO_4 \cdot 5H_2O$  (10 mol%), NaHCO<sub>3</sub> (20 mol%), and ascorbic acid (20 mol%) were dissolved in THF (30 mL)/water (6 mL) under a nitrogen atmosphere in a Schlenk flask. After the mixture was stirred at 25-30°C under a nitrogen atmosphere for 8 h, the reaction was stopped by the addition of water, extracted with CHCl<sub>3</sub>, and washed with brine. The organic layer was dried over anhydrous magnesium sulfate and purified by column chromatography on silica gel (EtOAc/CHCl<sub>3</sub> (2:1, v/v) as eluent to afford G1-PFPh-N as a red solid (1.42 g, 86.6%).  $^1\!H\,NMR$ (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 2.24$  (br s; CH<sub>2</sub>), 2.94 (br s; CH<sub>2</sub>C), 3.63 (br s; NCH<sub>2</sub>), 3.92 (br s; NCH<sub>2</sub>), 4.16 (br s; NCH<sub>2</sub>), 4.31 (br s, 4H; OCH<sub>2</sub>), 4.60 (br s; COOCH<sub>2</sub>), 6.52 (d, J=7.8 Hz; ArH), 6.73 (t; ArH), 6.86 (d, J=8.4 Hz; ArH), 7.14 (m; ArH and C=CH), 7.63 (m; ArH), 7.79–7.90 ppm (m; ArH);  ${}^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 21.69$ , 28.44, 47.28, 49.57, 51.48, 63.31, 68.54, 109.16, 111.80, 112.73, 116.28, 117.33, 118.34, 122.08, 125.98, 129.62, 135.95, 139.29, 143.71, 145.10, 145.80, 146.66, 146.84, 148.36, 149.94, 155.16, 158.77 ppm; IR (KBr):  $\tilde{\nu} =$ 1740 (C=O), 1516, 1338 cm<sup>-1</sup> (NO<sub>2</sub>); MS (MALDI-TOF): *m/z* calcd for C<sub>80</sub>H<sub>57</sub>F<sub>20</sub>N<sub>15</sub>O<sub>14</sub>: 1854.4 [M+Na]<sup>+</sup>; found: 1853.8; elemental analysis calcd (%) for  $C_{80}H_{57}F_{20}N_{15}O_{14}$ : C 52.44, H 3.14, N 11.47; found: C 52.97, H 3.22, N 11.30.

Synthesis of dendrimer G1==PFPh-N: Diazonium salt 2 (181.8 mg, 0.57 mmol) and dendrimer G1-PFPh-N (696.3 mg, 0.38 mmol) were dissolved in DMF (5 mL) at 0 °C. The reaction mixture was stirred for 40 h at 0 °C, treated with water, extracted with CHCl<sub>3</sub>, 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/CHCl<sub>3</sub>, 2:1 v/v) to afford G1==PFPh-N as a red solid (624.3 mg, 79.6 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 2.02$  (s; C=CH), 2.16 (br s; CH<sub>2</sub>), 2.24 (br s; CH<sub>2</sub>), 2.48 (br s; CH<sub>2</sub>), 2.95 (br s; CH<sub>2</sub>C), 3.76 (br s; NCH<sub>2</sub>), 3.92 (br s; NCH<sub>2</sub>), 4.15 (br s; NCH<sub>2</sub>), 4.30 (br s, 4H; OCH<sub>2</sub>), 4.42 (br s, 4H; OCH<sub>2</sub>), 4.60 (br s; COOCH<sub>2</sub>), 6.58 (d, *J*=6.9 Hz; ArH), 6.86 (d, *J*=7.5 Hz; ArH), 7.31 (br s; ArH), 7.59 (m; ArH and C=CH), 7.74–7.87 ppm (m; ArH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 14.99$ , 21.70, 27.92, 28.34, 47.18, 49.58, 51.20, 63.29, 68.00,

68.54, 69.20, 83.08, 107.47, 109.17, 111.77, 116.30, 117.33, 122.27, 125.99, 135.91, 139.35, 141.66, 143.73, 145.03, 146.59, 147.10, 148.31, 149.94, 155.11, 158.80 ppm; IR (KBr):  $\tilde{\nu}$ =3290 (C=CH), 1740 (C=O), 1516, 1338 cm<sup>-1</sup> (NO<sub>2</sub>); MS (MALDI-TOF): *m*/*z* calcd for C<sub>91</sub>H<sub>66</sub>F<sub>20</sub>N<sub>18</sub>O<sub>17</sub>: 2085.5 [*M*+Na]<sup>+</sup>; found: 2085.9.

Synthesis of dendrimer G2-PFPh-N: The procedure was similar to the synthesis of dendrimer G1-PFPh-N with G1-≡-PFPh-N (454.0 mg, 0.22 mmol) and N,N-bis(2-azidoethyl)aniline (1; 23.1 mg, 0.10 mmol). The crude product was purified by column chromatography on silica gel (THF/CHCl<sub>3</sub>, 1:1 v/v) to afford G2-PFPh-N as a red solid (416 mg, 95.5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 2.21$  (br s: CH<sub>3</sub>), 2.93 (br s; CH<sub>2</sub>C), 3.64 (br s; NCH<sub>2</sub>), 3.74 (br s; NCH<sub>2</sub>), 3.91 (br s; NCH<sub>2</sub>), 4.11 (br s; NCH<sub>2</sub>), 4.40 (br s, 4H; OCH<sub>2</sub>), 4.59 (br s; COOCH<sub>2</sub>), 6.54 (br s; ArH), 6.70 (br s; ArH), 6.85 (br s; ArH), 7.14 (br s; ArH), 7.28 (m; ArH and C=CH), 7.45-7.90 ppm (m; ArH); 13C NMR (75 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 21.73$ , 28.37, 47.24, 49.62, 51.17, 63.33, 68.59, 109.23, 111.81, 116.33, 117.36, 122.35, 126.02, 129.63, 136.03, 139.52, 141.66, 143.85, 145.06, 146.63, 147.11, 148.34, 149.98, 155.16, 158.82 ppm; IR (KBr);  $\tilde{\nu} =$ 1738 (C=O), 1519, 1337 cm<sup>-1</sup> (NO<sub>2</sub>); MS (MALDI-TOF): m/z calcd for  $C_{192}H_{145}F_{40}N_{43}O_{34}$ : 4379.0 [*M*+Na]<sup>+</sup>; found: 4379.9; elemental analysis calcd (%) for C<sub>192</sub>H<sub>145</sub>F<sub>40</sub>N<sub>43</sub>O<sub>34</sub>: C 52.91, H 3.35, N 13.82; found: C 53.63, H 3.05, N 13.44.

Synthesis of dendrimer G2-=-PFPh-N: The procedure was similar to the synthesis of dendrimer G1-≡-PFPh-N with diazonium salt 2 (50.0 mg, 0.156 mmol) and dendrimer G2-PFPh-N (340.0 mg, 0.078 mmol). The reaction time was 5 days. The crude product was purified by column chromatography on silica gel (THF/CHCl<sub>3</sub>, 1:1 v/v) to afford G2-=-PFPh-N as a red solid (205.3 mg, 57.3 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta =$ 2.01 (s; C=CH), 2.20 (br s; CH<sub>2</sub>), 2.92 (br s; CH<sub>2</sub>C), 3.76 (br s; NCH<sub>2</sub>), 3.91 (br s; NCH<sub>2</sub>), 4.10 (br s; NCH<sub>2</sub>), 4.28 (br s, 4H; OCH<sub>2</sub>), 4.40 (br s, 4H; OCH<sub>2</sub>), 4.59 (br s; COOCH<sub>2</sub>), 6.51 (br s; ArH), 6.60 (br s; ArH), 6.84 (br s; ArH), 7.30 (br s; ArH), 7.42-7.58 (m; ArH and C=CH), 7.67-7.84 ppm (m; ArH);  ${}^{13}$ C NMR (150 M, CDCl<sub>3</sub>, 298 K):  $\delta = 21.95$ , 28.19, 28.60, 29.93, 47.53, 49.89, 51.45, 63.60, 68.71, 107.58, 109.39, 112.03, 116.62, 117.60, 122.70, 126.32, 137.11, 138.80, 142.81, 144.58, 144.93, 145.26, 146.62, 146.82, 147.36, 148.53, 149.58, 150.22, 155.37, 159.13 ppm; IR (KBr):  $\tilde{v} = 3310$  (C=CH), 1739 (C=O), 1519, 1338 cm<sup>-1</sup> (NO<sub>2</sub>); MS (MALDI-TOF): m/z calcd for  $C_{203}H_{154}F_{40}N_{46}O_{37}$ : 4612  $[M+Na]^+$ ; found: 4613.

General procedure of the synthesis of G3-PFPh-N, G4-PFPh-N, and G5-PFPh-N: A mixture of G2-8N<sub>3</sub>-N (1.00 equiv), different end-capped dendrons (9.00 equiv), and CuBr (8.00 equiv), was dissolved in DMF (0.02 M N<sub>3</sub>) under a nitrogen atmosphere in a Schlenk flask and N,N,N,N-pentamethyldiethylenetriamine (PMDETA; 8.00 equiv) was added. After the mixture had been stirred at 25–30 °C for 6 h, the reaction was stopped by the addition of water. The precipitate was washed repeatedly with water and further purified by repeated precipitation of their solutions in THF or CHCl<sub>3</sub> with EtOAc, filtered, washed with a large volume of EtOAc, and dried under vacuum at 40°C to a constant weight.

**G3-PFPh-N: G2-8N<sub>3</sub>-N** (30.1 mg, 0.010 mmol) and **G0-=PFPh-N** (72.1 mg, 0.090 mmol). **G3-PFPh-N** was obtained as a red powder (80.0 mg, 85.0 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ =1.8–2.4 (CH<sub>2</sub>), 2.8–3.1 (CH<sub>2</sub>C and CH<sub>2</sub>), 3.6–4.2 (NCH<sub>2</sub>), 4.3–4.7 (OCH<sub>2</sub> and COOCH<sub>2</sub>), 6.4–6.6 (ArH), 6.7–6.9 (ArH), 7.2–7.9 ppm (ArH and C=CH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ =22.05, 28.66, 29.88, 47.56, 49.90, 51.34, 63.62, 69.03, 107.65, 109.64, 112.13, 116.58, 117.61, 122.74, 126.24, 137.10, 138.79, 142.71, 144.90, 145.34, 146.62, 148.55, 149.69, 150.33, 155.41, 159.04 ppm; IR (KBr):  $\tilde{\nu}$ =1737 (C=O), 1518, 1338 cm<sup>-1</sup> (NO<sub>2</sub>); elemental analysis calcd (%) for C<sub>416</sub>H<sub>321</sub>F<sub>80</sub>N<sub>99</sub>O<sub>74</sub>: C 53.09, H 3.44, N 14.74; found: C 51.81, H 3.23, N 14.57.

**G4-PFPh-N: G2-8N<sub>3</sub>-N** (15.0 mg, 0.005 mmol) and **G1==PFPh-N** (92.9 mg, 0.045 mmol). **G4-PFPh-N** was obtained as a red powder (70.4 mg, 72.1 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ =1.4–2.0 (CH<sub>2</sub>), 2.1–2.3 (CH<sub>2</sub>), 2.8–3.1 (CH<sub>2</sub>C and CH<sub>2</sub>), 3.6–4.2 (NCH<sub>2</sub>), 4.3–4.7 (OCH<sub>2</sub> and COOCH<sub>2</sub>), 6.4–6.6 (ArH), 6.7–6.9 (ArH), 7.2–7.9 ppm (ArH and C=CH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ =22.14, 28.65, 43.10, 47.62, 49.89, 63.63, 68.85, 107.58, 109.46, 112.04, 116.54, 117.53, 122.89, 126.29, 137.08, 138.73, 142.80, 144.93, 145.23, 146.63, 148.44, 150.27 ppm; IR

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 $\begin{array}{l} (KBr): \ \tilde{\nu} = 1737 \ (C\!=\!\!O), \ 1517, \ 1339 \ cm^{-1} \ (NO_2); \ elemental \ analysis \ calcd \\ (\%) \ for \ C_{864}H_{673}F_{160}N_{211}O_{154}: \ C \ 53.18, \ H \ 3.48, \ N \ 15.14; \ found: \ C \ 52.99, \\ H \ 3.62, \ N \ 14.47. \end{array}$ 

**G5-PFPh-N: G2–8N<sub>3</sub>-N** (6.0 mg, 0.002 mmol) and **G2–=PFPh-N** (82.6 mg, 0.018 mmol). **G5-PFPh-N** was obtained as a red powder (63.1 mg, 79.5 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 1.6–2.5 (CH<sub>2</sub>), 2.6–3.1 (CH<sub>2</sub>C and CH<sub>2</sub>), 3.4–4.2 (NCH<sub>2</sub>), 4.3–4.8 (OCH<sub>2</sub> and COOCH<sub>2</sub>), 6.2–6.9 (ArH), 7.0–7.9 ppm (ArH and C=CH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 22.05, 28.66, 49.87, 63.64, 68.82, 107.65, 109.38, 111.98, 116.59, 117.53, 126.32, 137.11, 138.78, 144.92, 146.66, 148.42, 155.37, 159.09 ppm; IR (KBr):  $\tilde{\nu}$  = 1737 (C=O), 1516, 1337 cm<sup>-1</sup> (NO<sub>2</sub>); elemental analysis calcd (%) for C<sub>1760</sub>H<sub>1377</sub>F<sub>320</sub>N<sub>435</sub>O<sub>314</sub>: C 53.22, H 3.49, N 15.34; found: C 53.35, H 3.88, N 14.83.

Synthesis of dendrimer G1-=-PFPh-NS: The procedure was similar to the synthesis of dendrimer G1=-PFPh-N with diazonium salt 3 (173.9 mg, 0.54 mmol) and dendrimer G1-PFPh-N (659.7 mg, 0.36 mmol). The reaction time was 2 days. The crude product was purified by column chromatography on silica gel (EtOAc) to afford G1-≡-PFPh-NS as a red solid (654.1 mg, 86.6 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 1.98$  (m; CH<sub>2</sub>C), 2.05 (s; C=CH), 2.24 (br s; CH<sub>2</sub>), 2.33 (br s; CH<sub>2</sub>), 2.96 (br s; CH<sub>2</sub>C), 3.26 (br s; SCH<sub>2</sub>) 3.75 (br s; NCH<sub>2</sub>), 3.92 (br s; NCH<sub>2</sub>), 4.14 (br s; NCH<sub>2</sub>), 4.39 (br s; OCH<sub>2</sub>), 4.60 (br s; COOCH<sub>2</sub>), 6.56 (d; ArH), 6.86 (d, J = 7.2 Hz; ArH), 7.23 (s; C=CH), 7.61–7.96 ppm (m; ArH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 298 K): δ=13.92, 17.00, 21.54, 28.27, 47.03, 49.44, 50.96, 54.80, 60.15, 63.24, 68.42, 70.03, 81.62, 107.22, 109.00, 111.67, 116.16, 117.15, 122.20, 122.73, 125.88, 128.81, 135.88, 139.24, 141.57, 143.64, 144.86, 146.46, 146.99, 148.13, 149.33, 149.94, 155.00, 155.60, 158.68 ppm; IR (KBr):  $\tilde{v} = 3289$  (C=CH), 1716 (C=O), 1514, 1338 (NO<sub>2</sub>), 1140 cm<sup>-1</sup> (SO<sub>2</sub>); MS (MALDI-TOF): m/z calcd for  $C_{91}H_{67}F_{20}N_{17}O_{16}S$ : 2088.4 [*M*+Na]<sup>+</sup>; found: 2088.8.

Synthesis of dendrimer G2-PFPh-N: The procedure was similar to the synthesis of dendrimer G1-PFPh-N with dendrimer G1-≡-PFPh-NS (454.7 mg, 0.22 mmol) and N,N-bis(2-azidoethyl)aniline (1; 23.1 mg, 0.10 mmol). The crude product was purified by column chromatography on silica gel (THF/CHCl<sub>3</sub>, 1:1 v/v) to afford G2-PFPh-NS as a red solid (425.8 mg, 97.5 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 1.83$  (br s; CH<sub>2</sub>), 2.05 (br s; CH<sub>2</sub>), 2.23 (br s; CH<sub>2</sub>C), 2.78 (br s; CH<sub>2</sub>C), 2.94 (br s; CH<sub>2</sub>C), 3.13 (br s; SCH<sub>2</sub>), 3.62 (br s; NCH<sub>2</sub>), 3.73 (br s; NCH<sub>2</sub>), 3.92 (br s; NCH<sub>2</sub>), 4.14 (br s; NCH<sub>2</sub>), 4.39 (br s; OCH<sub>2</sub>), 4.59 (br s; COOCH<sub>2</sub>), 5.59 (s; NCH<sub>2</sub>), 6.59 (br s; ArH), 6.84 (br s; ArH), 7.16 (s; C=CH), 7.62 (m; ArH), 7.77-8.00 ppm (m; ArH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 298 K):  $\delta \!=\! 21.63,\, 22.00,\, 22.43,\, 23.64,\, 27.64,\, 28.33,\, 47.11,\, 49.53,\, 51.02,\, 55.10,\, 63.31,$ 68.45, 109.16, 111.78, 112.81, 116.29, 117.29, 122.28, 122.80, 125.97, 128.88, 129.69, 135.94, 139.37, 143.75, 144.40, 144.98, 145.84, 146.61, 147.07, 148.24, 149.34, 150.00, 155.07, 158.78 ppm; IR (KBr): v=1738 (C=O), 1504, 1332 (-NO<sub>2</sub>), 1142 cm<sup>-1</sup> (SO<sub>2</sub>); MS (MALDI-TOF): m/z calcd for C192H147F40N41O32S2: 4387 [M+Na]+; found: 4388; elemental analysis calcd (%) for  $C_{192}H_{147}F_{40}N_{41}O_{32}S_2{\rm :}\ C\,52.48,\ H\,3.39,\ N\,13.16;$  found: C 52.90, H 3.56, N 12.76.

Synthesis of dendrimer G2-=-PFPh-NS: The procedure was similar to the synthesis of dendrimer G1==-PFPh-N with diazonium salt 2 (51.2 mg, 0.16 mmol) and dendrimer G2-PFPh-NS (349.2 mg, 0.08 mmol). The reaction time was 6 days. The crude product was purified by column chromatography on silica gel (THF/CHCl<sub>3</sub>, 2:1 v/v) to afford G1-=-PFPh-NS as a red solid (229.1 mg, 62.3 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta =$ 2.01 (s, C=CH), 2.10 (m; CH $_2$  and CH $_2$ C), 2.22 (m; CH $_2),$  2.48 (m; CH<sub>2</sub>C), 2.82 (m; CH<sub>2</sub>C), 2.94 (m; CH<sub>2</sub>C), 3.13 (t, J=4.0 Hz; SCH<sub>2</sub>), 3.73 (br s; NCH<sub>2</sub>), 3.91 (br s; NCH<sub>2</sub>), 4.12 (br s; NCH<sub>2</sub>), 4.30 (br s; CH<sub>2</sub>), 4.44 (br s; OCH<sub>2</sub>), 4.59 (t, J=8.0 Hz; COOCH<sub>2</sub>), 6.54 (d, J=8.0 Hz; ArH), 6.69 (d, J=8.0 Hz; ArH), 6.84 (d, J=8.0 Hz; ArH), 7.61 (m; ArH and C=CH), 7.70-7.90 ppm (m; ArH); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 21.99, 23.98, 28.63, 47.48, 49.89, 51.43, 63.61, 68.75, 107.58, 109.42,$ 112.10, 116.68, 117.66, 122.59, 126.37, 138.83, 144.93, 146.69, 147.41, 148.60, 150.22, 155.39, 159.13, 160.87 ppm; IR (KBr):  $\tilde{\nu} = 3289$  (C=CH), 1738 (C=O), 1514, 1335 (NO<sub>2</sub>), 1142 cm<sup>-1</sup> (SO<sub>2</sub>); MS (MALDI-TOF): *m*/ z calcd for  $C_{203}H_{156}F_{40}N_{44}O_{35}S_2$ : 4618 [*M*+Na]<sup>+</sup>; found: 4618.

General procedure of the synthesis of G3-PFPh-NS, G4-PFPh-NS, and G5-PFPh-NS: A mixture of the corresponding azide-containning core,

suitable end-capped dendrons, and CuBr (1.00 equiv) was dissolved in DMF ( $0.02 \text{ M} \text{ N}_3$ ) under a nitrogen atmosphere in a Schlenk flask and *N*,*N*,*N*,*N*,*N*-pentamethyldiethylenetriamine (PMDETA; 1.00 equiv) was added. After the mixture had been stirred at 25–30 °C for 6 h, the reaction was stopped by the addition of water. The precipitate was washed repeatedly with water and further purified by repeated precipitation of their solutions in THF or CHCl<sub>3</sub> with EtOAc, filtered, washed with a large volume of EtOAc, and dried under vacuum at 40 °C to a constant weight.

**G3-PFPh-NS: G1-4N<sub>3</sub>-N** (10.2 mg, 0.0088 mmol) and **G1==PFPh-NS** (80.0 mg, 0.0387 mmol). **G3-PFPh-NS** was obtained as a red powder (58.2 mg, 70.2 %). <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO, 298 K):  $\delta = 1.7-2.2$  (CH<sub>2</sub>), 2.7–3.1 (CH<sub>2</sub>C), 3.6–3.8 (NCH<sub>2</sub>), 3.8–4.0 (NCH<sub>2</sub>), 4.1–4.2 (NCH<sub>2</sub>), 4.2–4.6 (CH<sub>2</sub>O and CH<sub>2</sub>COO), 6.4–6.8 (ArH), 6.9–7.2 (ArH), 7.3–8.2 ppm (ArH); IR (KBr):  $\tilde{\nu} = 1738$  (C=O), 1516, 1332 (NO<sub>2</sub>), 1142 cm<sup>-1</sup> (SO<sub>2</sub>); elemental analysis calcd (%) for C<sub>416</sub>H<sub>325</sub>F<sub>80</sub>N<sub>95</sub>O<sub>70</sub>S<sub>4</sub>: C 53.03, H 3.48, N 14.12; found: C 52.71, H 3.68, N 13.66.

**G4-PFPh-NS: G1-4**N<sub>3</sub>**-S** (4.1 mg, 0.0035 mmol) and **G2**-**=**-**PFPh-NS** (70.8 mg, 0.0154 mmol). **G4-PFPh-NS** was obtained as a red powder (55.8 mg, 81.6%). <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO, 298 K):  $\delta$ =1.7–2.2 (CH<sub>2</sub>), 2.8–3.0 (CH<sub>2</sub>C), 3.8–4.0 (NCH<sub>2</sub>), 4.1–4.2 (NCH<sub>2</sub>), 4.2–4.6 (CH<sub>2</sub>O and CH<sub>2</sub>COO), 6.5–6.8 (ArH), 6.9–7.0 (ArH), 7.4–8.0 (ArH). IR (KBr):  $\tilde{\nu}$ =1735 (C=O), 1516, 1337 (NO<sub>2</sub>), 1141 cm<sup>-1</sup> (SO<sub>2</sub>); elemental analysis calcd (%) for C<sub>864</sub>H<sub>673</sub>F<sub>160</sub>N<sub>201</sub>O<sub>144</sub>S<sub>10</sub>: C 53.09, H 3.52, N 14.40; found: C 53.63, H 3.86, N 13.94.

**G5-PFPh-NS: G2-8N<sub>3</sub>-NS** (4.5 mg, 0.0015 mmol) and **G2=PFPh-NS** (60.7 mg, 0.0132 mmol). **G5-PFPh-NS** was obtained as a red powder (43.2 mg, 72.4 %). <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO, 298 K):  $\delta$ =1.4–2.0 (CH<sub>2</sub>), 2.6–2.8 (CH<sub>2</sub>C), 3.6–4.0 (NCH<sub>2</sub>), 4.1–4.6 (NCH<sub>2</sub>, CH<sub>2</sub>O and CH<sub>2</sub>COO), 6.3–6.9 (ArH), 7.1–8.0 ppm (ArH); IR (KBr):  $\tilde{\nu}$ =1738 (C= O), 1517, 1332 (NO<sub>2</sub>), 1141 cm<sup>-1</sup> (SO<sub>2</sub>); elemental analysis calcd (%) for C<sub>1760</sub>H<sub>1397</sub>F<sub>320</sub>N<sub>415</sub>O<sub>294</sub>S<sub>20</sub>: C 53.13, H 3.54, N 14.61; found: C 53.57, H 3.87, N 13.99.

**Preparation of the polymer thin films**: The dendrimers were dissolved in THF (concentration: 4 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.

**NLO measurements of the 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 an angle of 45° to the incident beam and poled inside the oven; the intensity of SHG was monitored simultaneously. The poling conditions were as follows: *T*: different for each polymer (Table 2); V=7.5 kV at the needle point; gap distance: 0.8 cm. The SHG measurements were carried out by using a Nd:YAG laser that was 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 compound.

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