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The influence of pentafluorophenyl groups on the nonlinear optical (NLO) performance of high generation dendrons and dendrimers

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With the aim to make the influence of pentafluorophenyl groups in the periphery of high generation dendrons and dendrimers on their NLO performance clearly, some NLO dendrons and dendrimers with different chromophore moieties or different end-capped groups were carefully designed and investigated in detail. The results demonstrated that some strong Ar-Ar^F interactions between the pentafluorophenyl groups in the periphery and the normal phenyl rings of the donors, could influence the topological structures of dendrons or dendrimers, and then affect their NLO performance. Furthermore, the optical transparency and the stability of the dendrons and dendrimers with pentafluorophenyl groups as end-capped moieties were all improved, in comparison with normal dendrons and dendrimers containing phenyl ones as the end-capped groups.

Organic/polymeric second-order nonlinear optical (NLO) materials have continuously drawn great interest in the past decades, due to some advantages over inorganic crystals, such as their larger nonlinearity, better processability, ultrafast response time and superior chemical flexibility^{1–5}. To meet the requirements for the practical applications, mainly, three parameters (large optical nonlinearity, good optical transparency and excellent temporal stability of dipole orientation) are more important for scientists in the design of second-order NLO materials^{6–8}. In recent years, the fluorine (F) atoms (generally in pentafluorophenyl groups) were often introduced into NLO systems to improve their optical transparency and decrease their optical loss^{9–11}. The electronic activity of pentafluorophenyl group is much different from the normal phenyl one, and there are strong electrostatic interactions between the electron-poor pentafluorophenyl groups and electron-rich phenyl rings^{12–14}. Besides the improved optical transparency, larger NLO coefficients could be also achieved: in 2007, Jen and co-workers first developed a new class of molecular glasses by utilizing the reversible self-assembly of aromatic/perfluoroaromatic dendron-substituted NLO chromophores through the presence of these Ar-Ar^F interactions, which exhibited the improved poling efficiency and much enhanced macroscopic NLO effects^{15,16}. Recently, according to the site-isolation principle^{17,18} and our previous systematic work on the concept of “suitable isolation group”^{19,20}, this Ar-Ar^F self-assembly effect was further applied to macromolecules with dendritic structures (including hyperbranched polymers^{21,22} and dendrimers^{23,24}), and better NLO effects could be achieved while the pentafluorophenyl groups were in the periphery, accompanying with the improved optical transparency and stability.

However, at present, there were still some confusing factors in these dendritic structures. For example: in these dendrimers with pentafluorophenyl in the periphery, besides the chromophore moieties, there was no other phenyl rings, thus, how did the Ar-Ar^F self-assembly effect work? How did this Ar-Ar^F self-assembly effect improve the NLO coefficients? Could the above results be applied to all the NLO dendrimers? To make the influence of pentafluorophenyl groups in the periphery of high generation dendrons and dendrimers on their NLO performance more clearly, in this paper, we synthesized and investigated some NLO dendrons and dendrimers containing different chromophore or different end-capped groups, and the results demonstrated that the Ar-Ar^F self-assembly effect could be present between the pentafluorophenyl groups in the periphery and the normal phenyl rings of the donors. This effect, thus, could influence the topological structure of dendrons or dendrimers, and then affect their NLO coefficients.



Result and discussion

Totally, there were eight series of dendrons or dendrimers discussed in this paper, and their structures (the second generation ones as examples) were shown in Figure 1. To distinguish them, the name for dendrons was Gn-(Ph or PFPh)-(N or S); n was the generation of dendrons; Ph meant that the end-capped groups of this dendron were phenyl groups, while PFPh meant pentafluorophenyl groups in the periphery; N meant this dendron consisted of nitro-based azobenzene chromophore, while S for sulfonyl-based one. For example, G2-Ph-N was the third generation dendron containing nitro-based azobenzene chromophore with phenyl groups in the periphery; G4-PFPh-S was the fourth generation dendron bearing sulfonyl-based azobenzene chromophore with pentafluorophenyl groups in the periphery. Usually, the dendrons were conical, while the topological structure of dendrimers should be global-like²⁵. Thus, we added a “GL” (short for global-like) suffix for the names of dendrimers to differentiate the dendrons. For example, G2-PFPh-N-GL was the second generation dendrimer containing nitro-based azobenzene chromophore with pentafluorophenyl groups in the periphery; G3-Ph-S-GL was the third generation dendrimer bearing sulfonyl-based azobenzene chromophore with phenyl groups in the periphery.

As mentioned above, there were three main requirements in the design of second-order NLO materials: large optical nonlinearity, good optical transparency and excellent temporal stability of dipole

orientation. In this paper, their second-harmonic generation (SHG) coefficients (d_{33} values), maximum absorptions of thin films and the depoling behavior were used to characterize these three parameters of dendrons and dendrimers, with the results listed in Table 1 and Supplementary Table S5. It was obvious that the maximum absorptions in films were blue-shifted and the onset temperatures for decays in the d_{33} values were enhanced, accompanying with the introduced pentafluorophenyl moieties in the periphery instead of normal phenyl rings, meaning the Ar-Ar^F self-assembly effect could improve the optical transparency and stability of dipole orientation of dendrons and dendrimers (Figures S1–S2 and Figures S12–S15 used the highest generation dendrons and dendrimers as examples to illustrate this point). Thus, our discussions would focus on the influence of pentafluorophenyl groups on the NLO property. Generally, when testing the NLO coefficient, the errors were inevitable. Thus, to ensure the comparability of their NLO coefficient, the NLO coefficients of these dendrimers were measured by the same testing system and at the same time. Furthermore, we repeated the measurements at least three times for each sample, and calculated their averages.

The influence of the topological structure on NLO coefficient has attracted the attention of scientists very earlier. For example, to control the shape of the chromophore by the introduction of isolation groups has been proved to be an efficient approach to minimize the strong interactions among chromophore moieties and enhance the poling efficiency; and the spherical shape was considered as the most

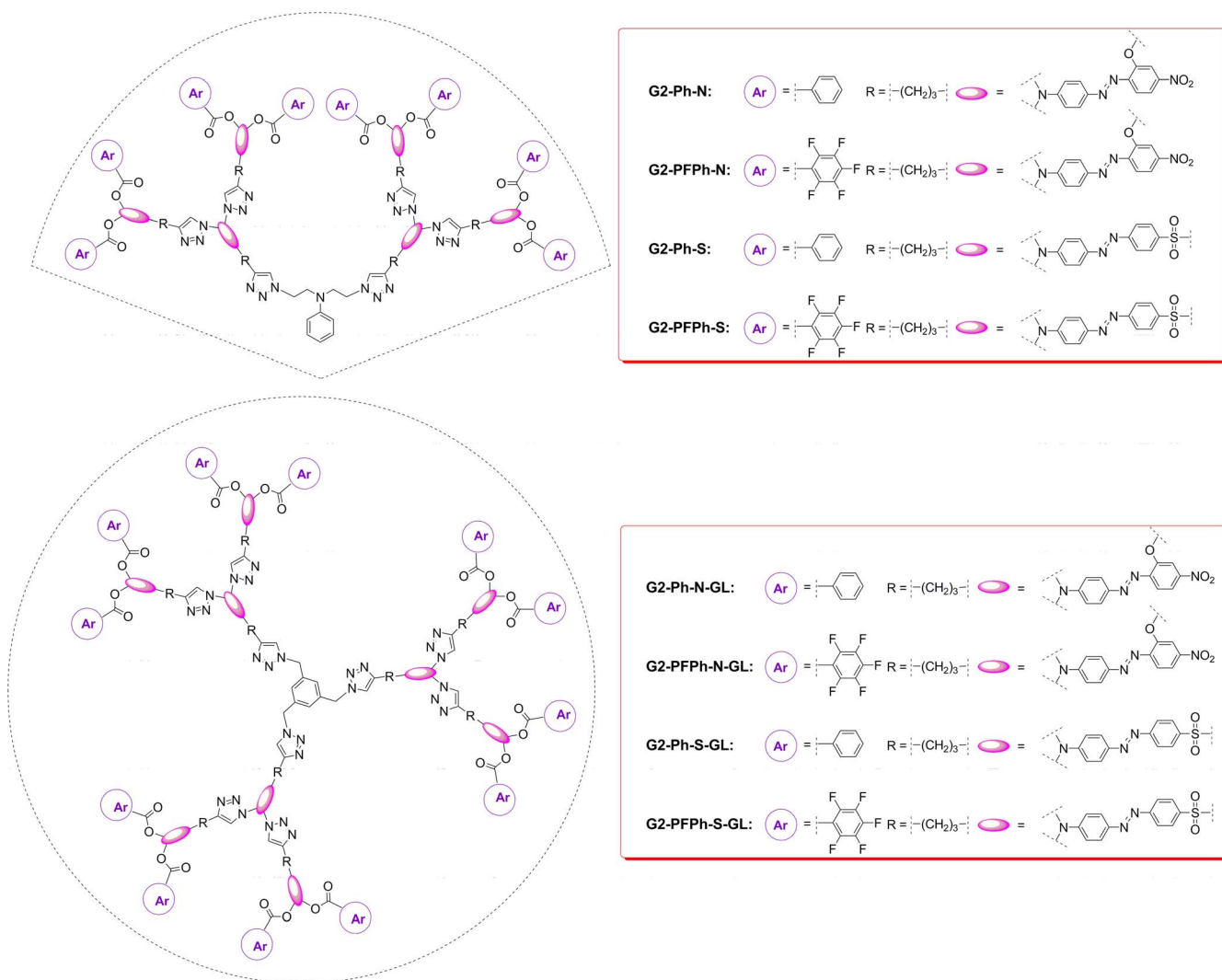


Figure 1 | The structure of the second generation dendrons or dendrimers.



Table 1 | Physical and NLO results of the highest generation dendrons and dendrimers

Compounds	T_g^a	T_d^b	T_e^c	l_s^d	d_{33}^e	$d_{33}^{(\infty)f}$	ϕ^g	N^h	λ_{max}^i	T_{onset}^j
no.	(°C)	(°C)	(°C)	(nm)	(pm/V)	(pm/V)			(nm)	(°C)
G5-Ph-N^k	125	275	138	170	193 ($\pm 10\%$)	34	0.31	0.544	470	107
G5-PFPh-N^k	165	233	135	210	206 ($\pm 10\%$)	42	0.34	0.466	460	111
G4-Ph-S^k	134	304	140	210	117 ($\pm 10\%$)	33	0.23	0.620	432	103
G4-PFPh-S	165	243	150	190	140 ($\pm 10\%$)	42	0.23	0.529	427	136
G4-Ph-N-GL^k	123	284	125	210	233 ($\pm 10\%$)	41	0.32	0.540	470	93
G4-PFPh-N-GL^k	128	239	140	170	252 ($\pm 10\%$)	52	0.35	0.460	460	107
G3-Ph-S-GL^k	(-) ^l	299	130	220	181 ($\pm 10\%$)	51	0.33	0.609	433	96
G3-PFPh-S-GL	(-) ^l	233	140	200	145 ($\pm 10\%$)	44	0.28	0.516	424	108

^aGlass transition temperature (T_g) of polymers detected by the DSC analyses under argon at a heating rate of 10°C/min.

^b5% weight loss temperature of polymers detected by TGA analyses under nitrogen at a heating rate of 10°C/min.

^cthe best poling temperature.

^dFilm thickness.

^eSecond harmonic generation (SHG) coefficient.

^fThe nonresonant d_{33} values calculated by using the approximate two-level model.

^gOrder parameter $\phi = 1 - A_1/A_0$, A_1 and A_0 are the absorbance of the polymer film after and before poling, respectively.

^hThe loading density of the effective chromophore moieties.

ⁱThe maximum absorption of dendrimers in films.

^jThe onset temperatures for decays in the d_{33} values.

^kTested in our previous work, ref: 23,24,38,41.

^lThere was not any inflection point from their DSC curve.

ideal conformation for the NLO property^{17,18,26}. Based on this point, many novel series of NLO dendronized polymers^{27–30}, hyper-branched polymers^{31–33}, and dendrimers^{34–36}, which had highly 3D branched structure with the isolation groups, were prepared and exhibited large NLO coefficients. Earlier in 2010, we have discussed the influence of generation number of dendrons. From G1-Ph-N to G5-Ph-N, accompanying with the growth of the dendrons, the topological structures became more and more ideal, and the d_{33} value also increased from 100 pm/V of G1-Ph-N to 193 pm/V of G5-Ph-N^{37,38}. Excitedly, this phenomenon has been observed in all of these dendrons and dendrimers, as shown in Table S5.

Once introducing the pentafluorophenyl moieties in the periphery instead of normal phenyl rings, in most cases, the d_{33} values of the resultant dendrons or dendrimers could be enhanced, for example, the d_{33} value of G5-PFPh-N was 206 pm/V, higher than that of G5-Ph-N. The only reason should be the presence of Ar-Ar^F electrostatic interactions. In order to confirm this point, their ¹⁹F NMR spectra were tested. From the chemical structure of these dendrimers, only three types of fluorine atoms should be distinguished from the pentafluorophenyl, correspondingly, in their ¹⁹F NMR spectra, there should be three kinds of peaks. However, if there were some Ar-Ar^F electrostatic interactions present in these dendrons or dendrimers, the environment of some fluorine atoms would be different from the previous status, resulting in the changed ¹⁹F NMR spectra. As shown in Figure 2, in the ¹⁹F NMR spectra of high generation dendrons and dendrimers, there were some small peaks appeared in addition to the three original peaks of pentafluorophenyl, indicating there should be some electrostatic interactions present. However, this result brought out another question: besides the chromophore moieties, there were no other phenyl rings, then how did these interactions exist? There might be the only possibility that the phenyl ring, which had the Ar-Ar^F electrostatic interactions with the pentafluorophenyl in the periphery of the dendrons and dendrimers, was the donor of the chromophore group, as only this phenyl ring was electron-rich. To confirm this possibility, the ¹⁹F NMR spectra of the dendrons and dendrimers with different types of chromophores were investigated. In comparison with nitro-based chromophore, the sulfonyl-based one had lower $\mu\beta$ value³⁹, indicating that the electron density of the donor of this kind of chromophore should be higher than that of nitro-based one. Thus, if our surmise was correct, the Ar-Ar^F electrostatic interactions in the dendrons and dendrimers containing sulfonyl-based azobenzene chromophore moieties should be stronger than those in nitro-based ones. It was the case. As shown in

Figure 2, it was easily seen that the signal intensity of new peaks derived from Ar-Ar^F electrostatic interactions of the dendrons and dendrimers containing sulfonyl-based azobenzene chromophore, were all stronger than those in nitro-based ones.

Why could these Ar-Ar^F self-assembly effect improved the NLO coefficients in most cases? There were two possible reasons: 1. the Ar-Ar^F self-assembly effect might exist in one dendrimer only, and these interactions could improve the topological structure, further make the shape of dendrons and dendrimer more like sphere, and then enhance their NLO effect; 2. the Ar-Ar^F self-assembly effect might exist between different molecules, and then some special arrangement of the dendrons and dendrimers would form, and further affect their macroscopic NLO coefficients. As shown in Figure 3, if the Ar-Ar^F self-assembly effect was the intramolecular one, in the low generation dendrons and dendrimers, due to such close distance, the presence of Ar-Ar^F electrostatic interactions must endure the twisted conformation. Thus, these interactions in high generation dendrons and dendrimers should be stronger than those in low generation ones. On the contrary, accompanying with the growth of dendrons and dendrimers, the amount of end-capped groups became more and more, which would act as a good isolated interface to “protect” the phenyl rings of the chromophore moieties. Therefore, if the Ar-Ar^F self-assembly effect was intermolecular interaction, it should be stronger in low generation dendrons and dendrimers rather than in high generation ones. Their ¹⁹F NMR spectra could also help us to distinguish them. In theory, the peak intensity in ¹⁹F NMR spectra was proportional to the amount of fluorine atoms. As shown in Figure 2, accompanying with the growth of dendrons and dendrimers, the signal intensity of new peaks from Ar-Ar^F electrostatic interactions became stronger and stronger, indicating that the Ar-Ar^F self-assembly effect became stronger and stronger, which was in consistent with the first surmise. Therefore, the Ar-Ar^F self-assembly effect should exist in one dendron or dendrimer itself, and accompanying with the growth of dendrons and dendrimers, these Ar-Ar^F self-assembly effects became stronger and stronger. This indicated that the topological structure was very important for these Ar-Ar^F electrostatic interactions. To confirm this, a control experiment has been conducted. Model molecule M1 was very similar to the Ar^F part of these dendrons and dendrimers in structure, while M2 was very similar to the Ar part of these dendrons and dendrimers (Figure 4). Therefore, if these Ar-Ar^F electrostatic interactions were really related to their topological structure, there should be not any additional peaks in

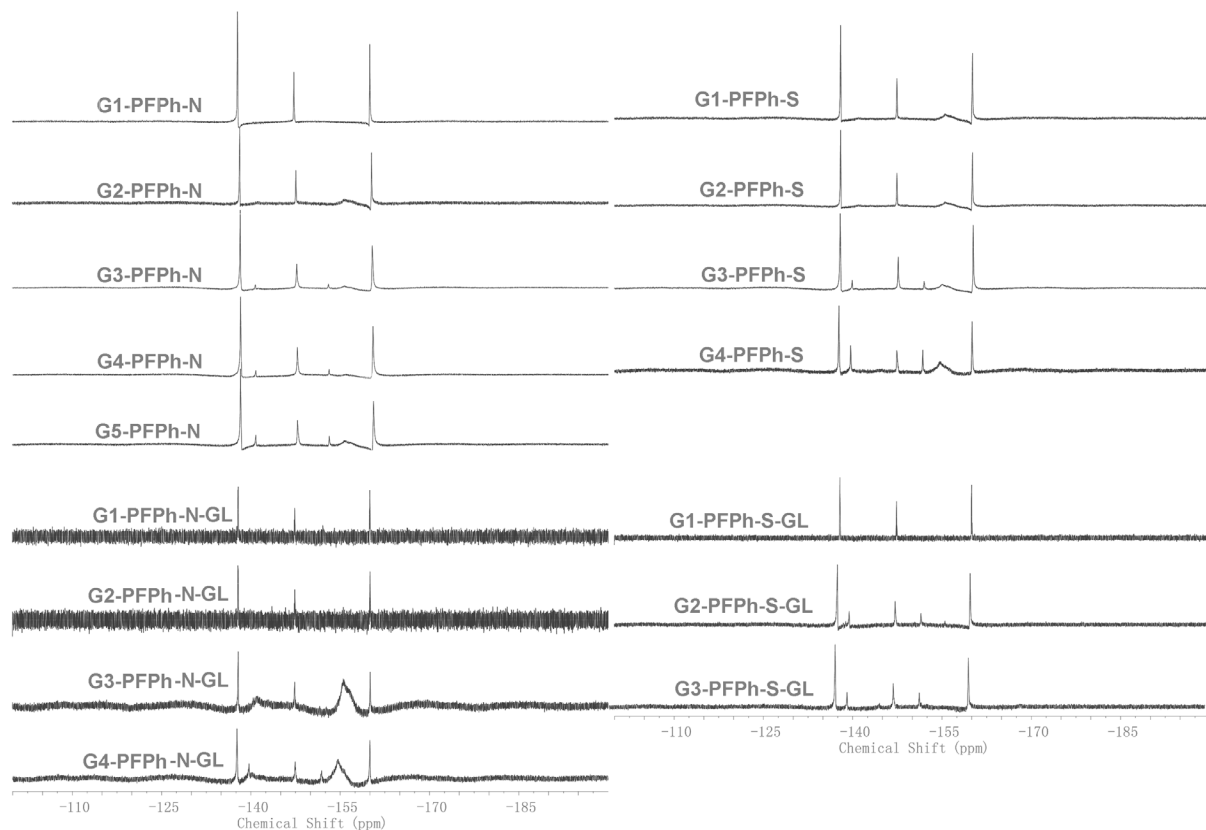
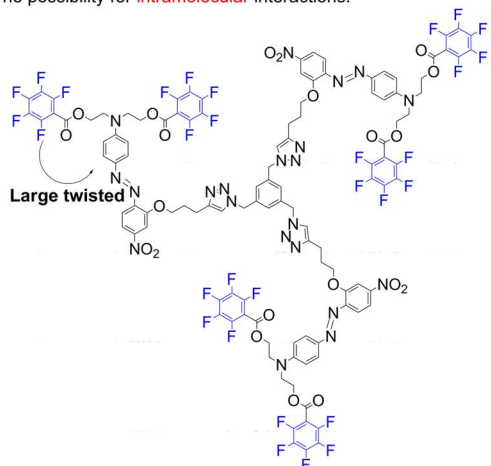


Figure 2 | The ^{19}F NMR spectra of the dendrons and dendrimers with pentafluorophenyl moieties in the periphery.

the ^{19}F NMR spectra of the M1 and M2 mixture under the same conditions, since M1 and M2 were only simple small molecules. Luckily, that was exactly what we did see: no matter we changed their ratio, concentration and solvent, there were only three peaks in

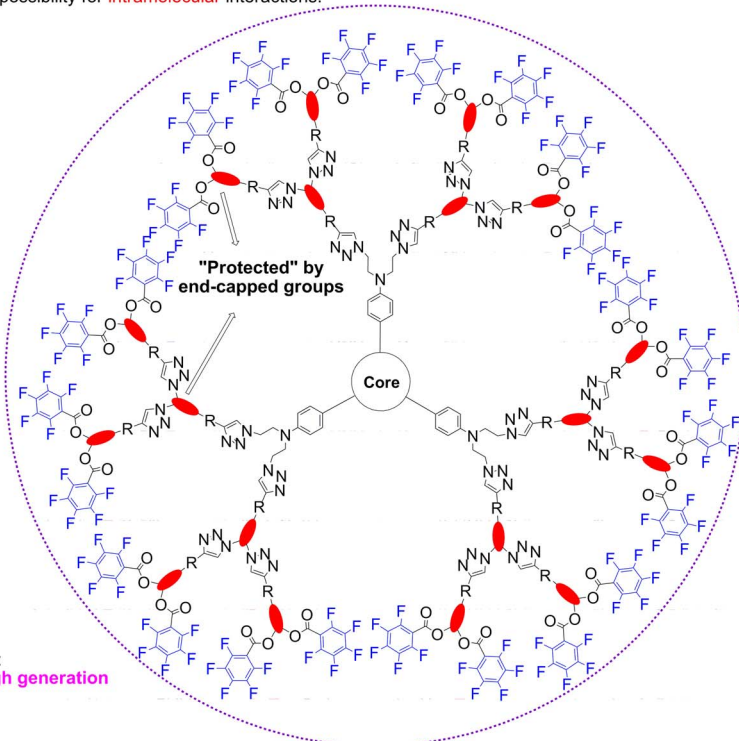
their ^{19}F NMR spectra, indicating that the Ar-Ar $^{\text{F}}$ electrostatic interactions between them were very weak, in consistent with our conclusion: these Ar-Ar $^{\text{F}}$ electrostatic interactions were also related to their topological structure.

The possibility for intramolecular interactions:



Strength for intramolecular interactions:
high generation stronger than low generation

The possibility for intramolecular interactions:



Strength for intermolecular interactions:
low generation stronger than high generation

Figure 3 | Two surmises for the Ar-Ar $^{\text{F}}$ electrostatic interactions in the dendrimers.

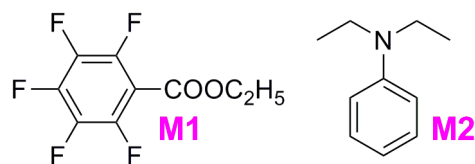


Figure 4 | The chemical structures of model molecules M1 and M2.

This surmise could also be partially confirmed by their gel permeation chromatography (GPC) results. First of all, it should be pointed out that the analysis by using linear polystyrenes as calibration standards, often underestimates the molecular weights of dendrimers with 3D branched structure, because of their quite different hydrodynamic radius⁴⁰. Therefore, their GPC results should be only used for comparison. It should point out that the same test concentrations were used to test their ¹⁹F NMR spectra and relative molecular mass by GPC technique. Thus, the similar Ar-Ar^F electrostatic interactions might be observed in their GPC results. If the second surmise was correct, there should be some dimmer or trimmer *et al.* in these compounds, thus, their GPC results should be higher than those of dendrons and dendrimers only with phenyl rings as end-capped groups. However, in comparison with dendrons and dendrimers with the same generation and chromophore moieties but phenyl rings in the periphery, the molecular weights of the dendrons and dendrimers with pentafluorophenyl moieties in the periphery were much lower, although their actual molecular weights were higher, indicating that these dendrimers were soluble in the solvents as single molecules. Thus, the first surmise should be the right one. The GPC results could also tell us the reason why these pentafluorophenyl moieties in the periphery were beneficial to the NLO effect. As mentioned above, the GPC results were related to the hydrodynamic radius of macromolecules, and if the shape of the tested molecule was more like sphere, its GPC result should be lower. Here, by the utilization of this special feature, the GPC results might be used to characterize the 3D branched structure of dendrons and dendrimers in some sense: if the difference between the tested and true values was bigger, its hydrodynamic radius should be more different from that of linear polymers, and its topological structure might be much closer to spherical (the ideal one for the NLO materials). A M_c/M_w value (M_c was the calculated molecular weight while M_w was the weight average molecular weight determined by GPC) was used to describe this difference, with the values listed in Table 2 and Supplementary Table S6. As expected, accompanying with the increasing generation of dendrimers, the M_c/M_w values were going higher, and the 3D branched structure should be improved, which was the most important reason for the enhancement of NLO coefficient. For example, the M_c/M_w value of G3-Ph-S-GL was 1.465 and its d_{33} value was 181 pm/V, while the M_c/M_w value of G1-Ph-S-GL was only 0.978 and its d_{33} value was 107 pm/V). Also, this point could explain the fact that the NLO coefficients of dendrimers were usually higher than their dendron analogues. For example, the M_c/M_w value of G3-Ph-S was only 1.322 and its d_{33} value was 103 pm/V, lower than those of G3-Ph-S-GL (1.465 and 181 pm/V). As shown in Tables 2 and S6, the M_c/M_w values of dendrons and dendrimers with pentafluorophenyl rings in the periphery were all higher than those of dendrons and dendrimers with normal phenyl rings in the periphery. Therefore, after the perfluoroaromatic rings were introduced into dendrons and dendrimers, especially in high generation ones (Table 2), the present Ar-Ar^F self-assembly effect between pentafluorophenyl rings in the periphery and the donor of chromophore moieties in the interior could improve their topological structure more like sphere (the ideal conformation for NLO materials). Thus, in most cases, the pentafluorophenyl groups in the periphery produced higher d_{33} values than the normal phenyl in the periphery. Also, accompanying with the improved topological structure, the site-isolation effect from the dendritic structure became stronger,

Table 2 | The GPC results of the highest generation dendrons and dendrimers

no.	M_w^a	M_w/M_n^a	M_c^b	M_c/M_w
G5-Ph-N	30300	1.36	33966	1.121
G5-PFPh-N	9300	1.10	39724	4.271
G4-Ph-S	9340	1.04	16728	1.791
G4-PFPh-S	7730	1.11	19606	2.536
G4-Ph-N-GL	10100	1.04	24851	2.461
G4-PFPh-N-GL	7090	1.33	29168	4.114
G3-Ph-S-GL	8150	1.10	11918	1.465
G3-PFPh-S-GL	7200	1.06	14077	1.955

^aDetermined by GPC in THF on the basis of a polystyrene calibration.

^b M_c was the calculated molecular weight.

which could play a key role in shielding the chromophore moieties from each other, and further resulted in the blue-shifted maximum absorptions with better optical transparency, to benefit their practical applications in photonics fields.

However, there was a defect by introducing pentafluorophenyl rings instead of normal phenyl rings in theory. The atomic weight of F atom was much higher than that of H atom, thus, the introduction of pentafluorophenyl rings instead of normal phenyl rings could improve the molecular weights of dendrons and dendrimers, and decrease the loading density of the effective chromophore moieties. Thus, there should be a balance present to tune up these two effects. If the effect of the decreased loading density of the effective chromophore moieties were stronger than the influence of the improved topological structure, the d_{33} value should decrease. In our investigation, this situation should only occur in two cases: low generation dendrons (or dendrimers) and high generation dendrimers. As discussed above, for the too highly twisted structure, the Ar-Ar^F self-assembly effect should be very weak in low generation dendrons and dendrimers. Thus, it was possible that the effect of the improvement of topological structure was weaker than the effect of the decreased loading density of the effective chromophore moieties. In high generation dendrimers, the topological structure might be already close to ideal, and could be only improved at a very limited degree by introducing pentafluorophenyl rings. And then, the decreased loading density of the effective chromophore moieties should be the main factor. Thus, the influence of the introduced pentafluorophenyl ring in the periphery of dendrons or dendrimers on NLO coefficient might be different, since different dendrons and dendrimers have different specific topological structures. Accompanying with the improvement of topological structure, the introduction of pentafluorophenyl ring in the periphery might decrease the d_{33} value first, and then improve the NLO coefficient, and at last, decrease the d_{33} value again.

Considering this, we compared their d_{33} values in detail in order to understand the effect of this Ar-Ar^F interaction deeply. The results could be easily seen in Figure 5. When the generation number was not larger than 3, the d_{33} values of Gn-PFPh-N were all a little lower than those of Gn-Ph-N. In these cases, the Ar-Ar^F self-assembly effect was weak, which could be confirmed by their ¹⁹F NMR spectra, and the decreased loading density of the effective chromophore moieties led to the lower d_{33} values of G1-PFPh-N to G3-PFPh-N. On the other hand, in our very recent work, it has been already determined that the topological structures of dendrons and dendrimers containing sulfonyl-based chromophore moieties should be more ideal than that of nitro-based ones as confirmed by their GPC results, because of the different linkage positions of the chromophore moieties in dendrons and dendrimers⁴¹. From the results, the most ideal topological structure among these dendrons and dendrimers should be Gn-Ph-S-GL and Gn-S-PFPh-GL. The comparison of these two series of dendrimers was shown in Figure 5. The d_{33} value of G1-



PFPh-S-GL was 119 pm/V, higher than 107 pm/V (G1-Ph-S-GL). However, in the second generation, the NLO coefficient of G2-PFPh-S-GL was 9 pm/V lower than that of G2-Ph-S-GL, and the difference was further enlarged to 36 pm/V in the third generation. The abnormal higher performance of G1-PFPh-S-GL than that of G1-Ph-S-GL was not clear, possibly indicating the complicated Ar-Ar^F self-assembly effect, some more work was needed to understand this effect more deeply. Except this case, all the other dendrons and dendrimers with pentafluorophenyl rings in the periphery had higher NLO coefficient than their analogues with phenyl rings with normal phenyl rings in the periphery. In these series of dendrimers, after introducing pentafluorophenyl rings in the periphery, the improvement of topological structure should be the main factor, thus, G4-PFPh-N-GL demonstrated the highest d_{33} value (252 pm/V) in all the dendrons and dendrimers discussed in this paper. It should be pointed out that, 252 pm/V should be the highest value so far for NLO materials, which contained only one type of simple azobenzene as chromophores.

As the films of these dendrons and dendrimers still had some absorptions at the wavelength of 532 nm (the doubled frequency of the 1064 nm fundamental wavelength), the NLO properties ($d_{33}(\infty)$) of dendrimers should be smaller (Table 1 and Supplementary Table S5), due to the resonant enhancement effect. As

expected, the trends of their $d_{33}(\infty)$ values were in consistent with their d_{33} values. Also, their order parameters (Φ) were measured to further explore the alignment of the chromophore moieties. As shown in Table 1 and Supplementary Table S5, the trends agreed with their d_{33} values once again, further confirming our conclusion.

It was very easy to consider that the Ar-Ar^F self-assembly effect could improve the temporal stability of dipole orientation, because additional energies should be required to overcome these Ar-Ar^F interactions to destroy the alignment of the chromophore moieties in the dendrons and dendrimers with pentafluorophenyl rings in the periphery. Here, depoling experiments were used to express their temporal stability of dipole orientation. The temperatures for decay in d_{33} values were listed in Table 1 and Supplementary Table S5. As expected, the dendrons and dendrimers with pentafluorophenyl rings in the periphery demonstrated better stability.

In summary, eight series of dendrons or dendrimers with different chromophore moieties or different end-capped groups were investigated systematically, by mainly utilizing their ¹⁹F NMR spectra, GPC results, optical transparency, second-order harmonic generation (SHG) coefficients. As a result, the effect of the Ar-Ar^F interactions in NLO dendritic structure should be very clear, and the main conclusions were listed as following:

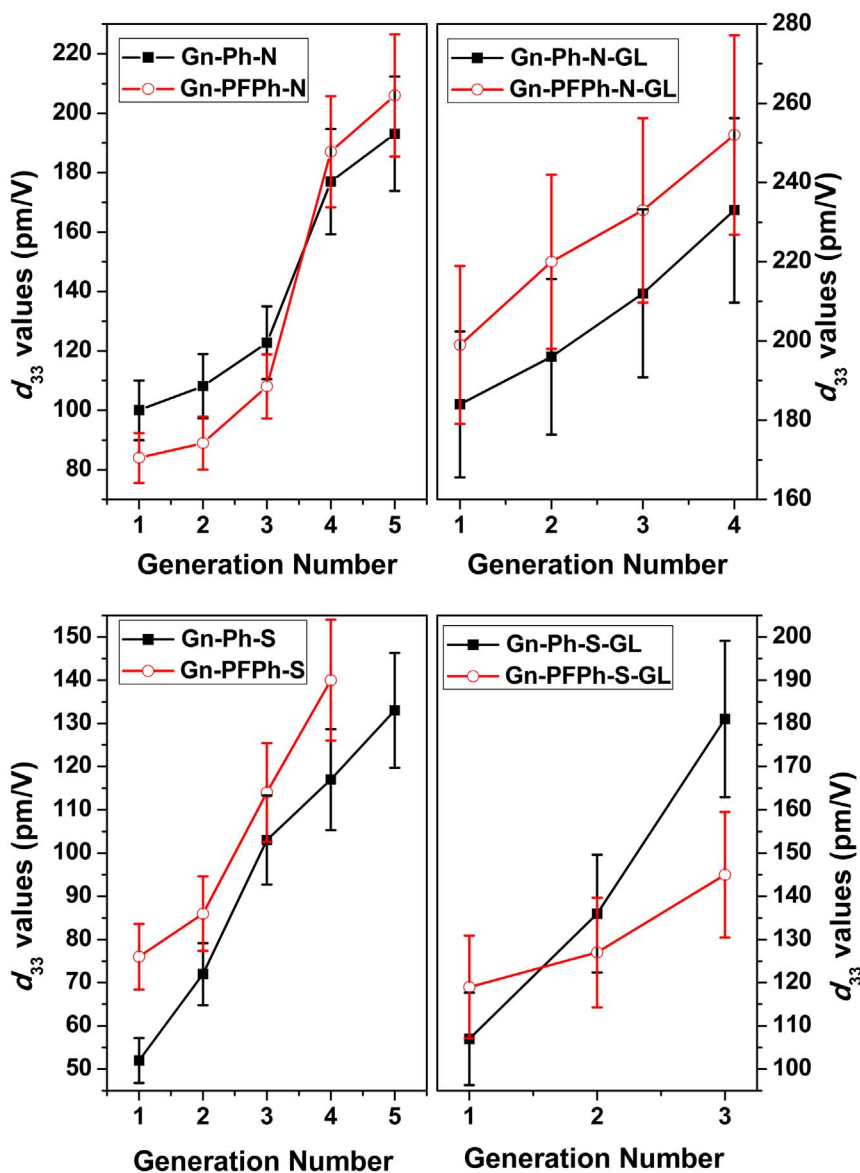


Figure 5 | The compare of the d_{33} values of NLO dendrons and dendrimers with different types of end-capped groups.



1. This type of Ar-Ar^F self-assembly effect should be intramolecular interactions between the pentafluorophenyl rings in the periphery and the donor parts in the interior. These interactions were related to the topological structures of the dendrons and dendrimers, and could also affect their topological structures;
2. The influence of this Ar-Ar^F self-assembly effect on their NLO performance in high generation dendrons and dendrimers was concerned on the topological structures of the dendrons and dendrimers. In most cases, this effect contributed to the NLO performance.
3. This Ar-Ar^F self-assembly effect could improve the optical transparency and stability of these dendrons and dendrimers.

Method

Synthesis. The synthetic route to these NLO dendrimers was first developed in 2010. At present, the synthetic procedure was very common to NLO dendrimers, some of them has been already prepared in our previous work^{23,24,38,41}. Supplementary Schemes S1–S7 and Tables S1–S4 was detailed synthetic route to each dendron or dendrimer.

Preparation of Thin Films. The dendrimers were dissolved in THF (concentration ~4 wt%), and the solutions were filtered through syringe filters, and the films were spin-coated onto indium-tin-oxide (ITO)-coated glass substrates, which were cleaned by *N,N*-dimethylformamide, acetone, distilled water and THF sequentially in 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 dendrimers was determined by in-situ second harmonic generation (SHG) experiment using a closed temperature controlled oven with optical windows and three needle electrodes. The films were kept at 45° to the incident beam and poled inside the oven, and the SHG intensity was monitored simultaneously. Poling conditions were as follows: temperature: different for each polymer (Supplementary Table S5); voltage: 7.5 kV at the needle point; gap distance: 0.8 cm. The SHG measurements were carried out with a Nd:YAG laser operating at a 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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Author contributions

Z.L. designed experiments, and provided funding. Z.L., Q.L. and J.Q. conceived the project. W.W. and C.W. performed the synthesis and characterization of the dendrimers. W.W. and C.Y. tested the NLO coefficients of these dendrimers. W.W. and Z.L. wrote the manuscript. All authors edited and commented on the manuscript.

Additional information

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