

Dendrimers with Large Nonlinear Optical Performance by Introducing Isolation Chromophore, Utilizing the Ar/Ar^F Self-Assembly Effect, And Modifying the Topological Structure

Wenbo Wu,[†] Cheng Ye,[‡] Jingui Qin,[†] and Zhen Li^{†,*}

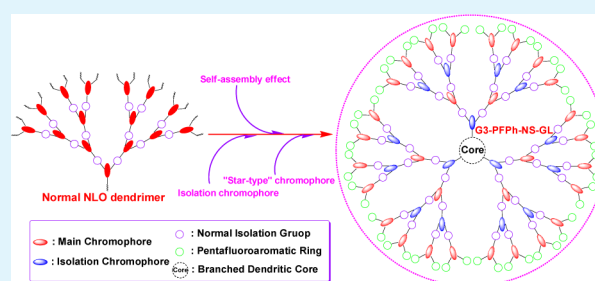
[†]Department of Chemistry, Hubei Key Lab on Organic and Polymeric Opto-Electronic Materials, Wuhan University, Wuhan 430072, China

[‡]Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, China

S Supporting Information

ABSTRACT: By the combination of divergent and convergent approach, a new series of NLO dendrimers (G1-PFPh-NS-GL to G3-PFPh-NS-GL) was conveniently prepared with satisfied yields through the powerful “click chemistry” reaction, in which perfluoroaromatic rings were introduced in the periphery, two types of chromophores were arranged with regular AB structure, and their topological structure was improved to a more spherical shape. All the dendrimers demonstrated good processability, and G1-PFPh-NS-GL exhibited the highest NLO effect of 221 pm/V among the three dendrimers.

KEYWORDS: nonlinear optical (NLO) materials, dendrimers, isolation chromophore, the Ar/Ar^F self-assembly effect, “star-type” chromophore



INTRODUCTION

Second-order nonlinear optical (NLO) materials have attracted considerable interest in the past decades because of their huge potential applications in different areas such as optical information processing, optical sensing, data storage, and telecommunications.^{1–3} In comparison with inorganic NLO crystals, organic NLO material have been put forth as promising candidates for the future NLO applications, because of their numerous advantages such as large nonlinearity, good processability, ultrafast response time, and superior chemical flexibility.^{4–10} In organic NLO field, the efficient translation of the large β 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- π -acceptor (D- π -A) structure make the pole-induced noncentrosymmetric alignment of chromophore moieties a daunting task during the poling process under an electric field.^{11,12} Fortunately, according to the experimental results and theoretical analysis, dendrimer (one kind of defect-free and perfectly monodisperse macromolecules with regular and highly branched three-dimensional structures)^{13–18} is considered as a very promising molecular topology for the next generation of highly efficient NLO materials, and expected to meet the basic requirements of practical applications (large macroscopic optical nonlinearity, high physical and chemical stability, and good optical transparency),^{19–21} because the three-dimensional (3D) structure, in which some isolation groups are bonded to the chromophore moieties, could decrease these strong intermo-

lecular dipole–dipole interactions, and increase the poling efficiency by utilizing the site isolation principle.^{22–28} In 2010, based on these excellent work, as well as our previous conclusions on the concept of “suitable isolation group”,^{29–35} our group designed and synthesized a series of NLO dendrimers G1 to G5 (see Schemes S1–S3 in the Supporting Information), which demonstrated excellent NLO activities (the d_{33} value of G5 was up to 193.1 pm/V, the highest value for simple azo chromophore moieties at that time).^{36,37}

On the other hand, besides site-isolation principle and the concept of “suitable isolation group”, there were some other methods proposed to enhance the NLO activities in recent years. In 2012, we used a chromophore with a lower $\mu\beta$ value as the isolation group for another chromophore with a higher $\mu\beta$ value to achieve high poling efficiency, as a result of the decreased strong electronic interactions, the NLO effect increased (see Chart S1 in the Supporting Information).³⁸ Also, the isolation chromophore have given good results in dendritic structure, including NLO hyperbranched polymers (see Scheme S4 in the Supporting Information) and dendrimers, if main chromophores were in the periphery and the two types of chromophores was with regular AB structure. The result showed that the introduction of isolation chromophore moieties into NLO materials could further improve their optical transparency and stability of polymers,

Received: April 9, 2013

Accepted: July 12, 2013

Published: July 26, 2013

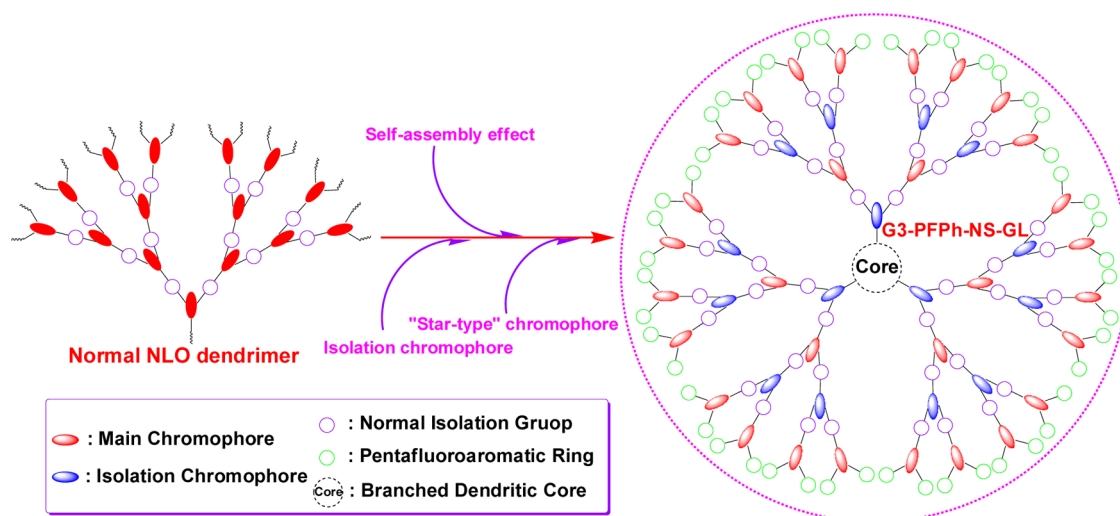


Figure 1. Graphical illustration of the original idea of paper and the structure of dendrimer G3-PFPh-NS-GL.

even the polymers containing “suitable isolation group”.^{39–43} Meanwhile, considering the electropositive activity of perfluorophenyl ring, by utilizing aromatic/perfluoroaromatic dendron-substituted NLO chromophores through the presence of the complementary Ar/Ar^F interactions, Jen and co-workers developed a new class of molecular glasses (see Charts S2 and S3 in the Supporting Information), which exhibited improved poling efficiency and greatly enhanced macroscopic NLO effects in 2007.^{44,45} In 2012, we improved the NLO linear polymers by introducing perfluorophenyl rings into NLO polymers as isolation groups, and the highest d_{33} value for linear polymers was achieved by using very simple azo chromophore (see Chart S4 in the Supporting Information).⁴⁶ This method was also used in dendritic structures (see Chart S5 in the Supporting Information), and the results showed that the use of pentafluorophenyl groups on the periphery of dendritic structure could produce higher d_{33} values than “normal” phenyl groups in the same positions.^{47–49} Also, there was another important parameter affecting the NLO coefficients: topological structure. As proposed by Jen, Dalton, and co-workers, spherical shape was the most ideal conformation.²² Accordingly, we modified the conical structure of dendrimers G1 to G5 to nearly spherical shape of (see Chart S6 and S7 and Scheme S5 in the Supporting Information), which exhibited higher NLO coefficients,⁵⁰ similar to those of “star-type chromophore”⁵¹ and “six-branched chromophore”.^{52,53} Then, if the above two other methods, the isolation chromophore and the self-assembly effect, could be also applied, perhaps better NLO performance could be achieved. However, till now, there was no example considering all of these three methods.

Therefore, in this paper, by combining these three methods, we attempted to design a new series of dendrimers of G1-PFPh-NS-GL to G1-PFPh-NS-GL (Figure 1), -PFPh indicates that their end-capped groups are pentafluorophenyl moieties; N is short for nitro-based azo chromophore, whereas S is short for sulfonyl-based azo chromophore, and -NS indicates that these two types of chromophores are regular arranged in these dendrimers; -GL means the topological structure of these dendrimers is global-like). Excitingly, these dendrimers showed very large NLO effect, and their d_{33} values were all higher than 200 pm/V. Also, their optical transparency and stability were both improved. Herein, we present the syntheses, characterization and properties of these new dendrimers in detail.

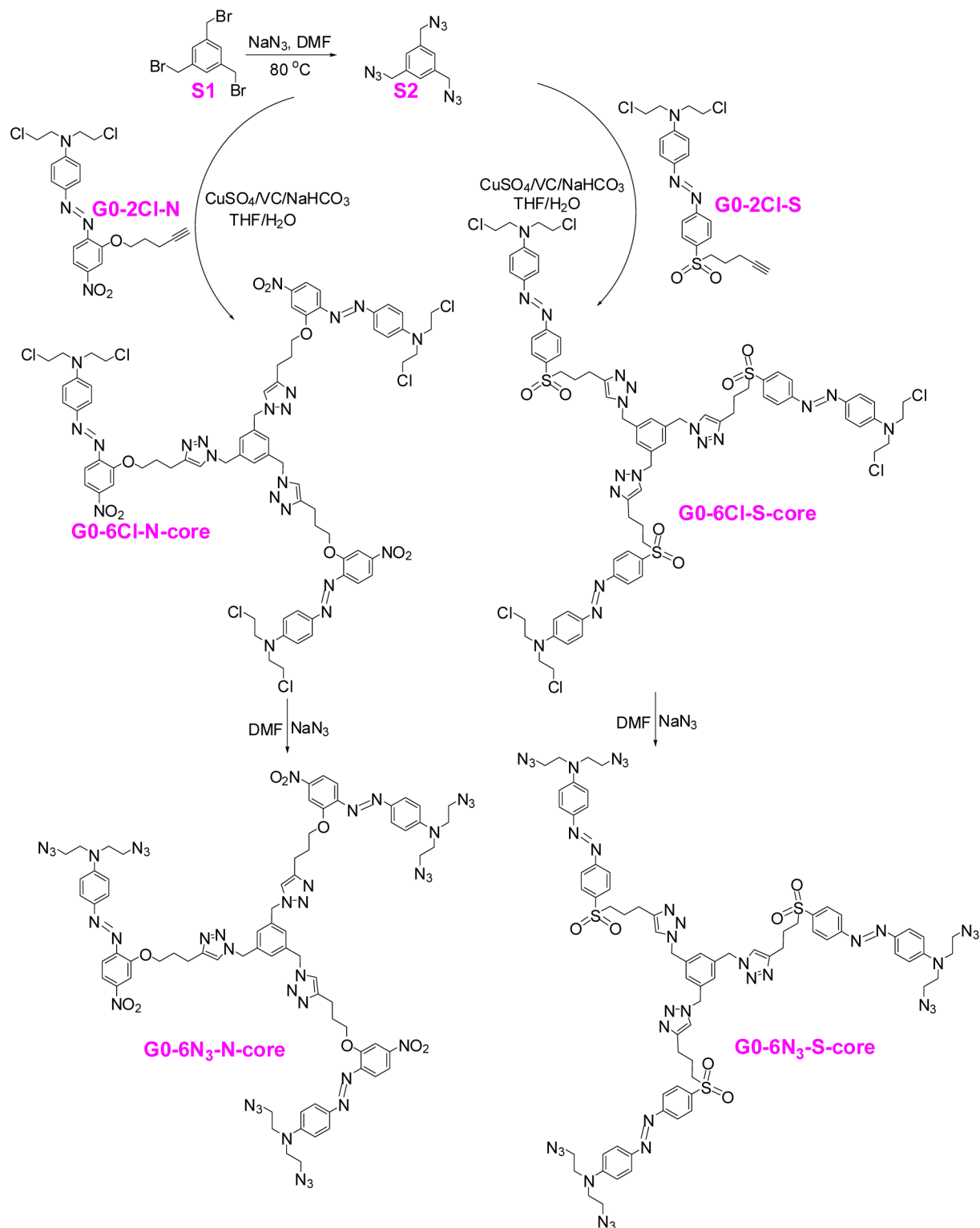
EXPERIMENTAL SECTION

Materials and Instrumentation. Tetrahydrofuran (THF) was dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen. *N,N*-Dimethylformamide (DMF) was dried over and distilled from CaH₂. The “star-type” chromophore cores G0-6N₃-N-core,⁴⁹ G0-6N₃-S-core,⁵⁴ (the suffix -core was used to differentiate the branched cores to the other dendrons or dendrimers) and the end-capped dendrons (Scheme 2, with the suffix -dendron to differentiate the other ones)⁴⁰ were synthesized according to our previous work by using the similar synthetic routes, and the detailed synthetic procedure was listed in the Supporting Information. *N,N,N,N,N*-Pentamethyldiethylenetriamine (PMDETA) was purchased from Alfa Aesar. All other reagents were used as received.

¹H, ¹³C, and ¹⁹F NMR spectra were measured on a Varian Mercury300, Varian Mercury600, or Bruker ARX400 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer-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 were measured on a Voyager-DE-STR MALDI-TOF mass spectrometer (MALDI-TOF MS; ABL, 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 microelemental analyzer. Gel permeation chromatography (GPC) was used to determine the molecular weights of dendrimers. 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. Thermal analysis was performed on NETZSCH STA449C thermal analyzer at a heating rate of 10 °C/min in nitrogen at a flow rate of 50 cm³/min 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. The thermometer for measurement of the melting point was uncorrected. The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

General Procedure of the Synthesis of G1-PFPh-NS-GL to G3-PFPh-NS-GL. A mixture of different azide-containing “star-type” chromophore core, suitable end-capped dendrons, and CuBr (1.00 equiv) were dissolved in DMF (0.02 M-N₃) under nitrogen in a Schlenk flask, then *N,N,N,N,N*-pentamethyldiethylenetriamine (PMDETA) (1.00 equiv) was added. After the mixture was stirred at 25–30 °C for 6 h, the reaction was stopped by the addition of water. The precipitate was washed with lots of water and further purified by repeating precipitations of their THF or CHCl₃ solutions into ethyl

Scheme 1. Synthetic Route to the “Star-Type” Chromophore Core of Dendrimers

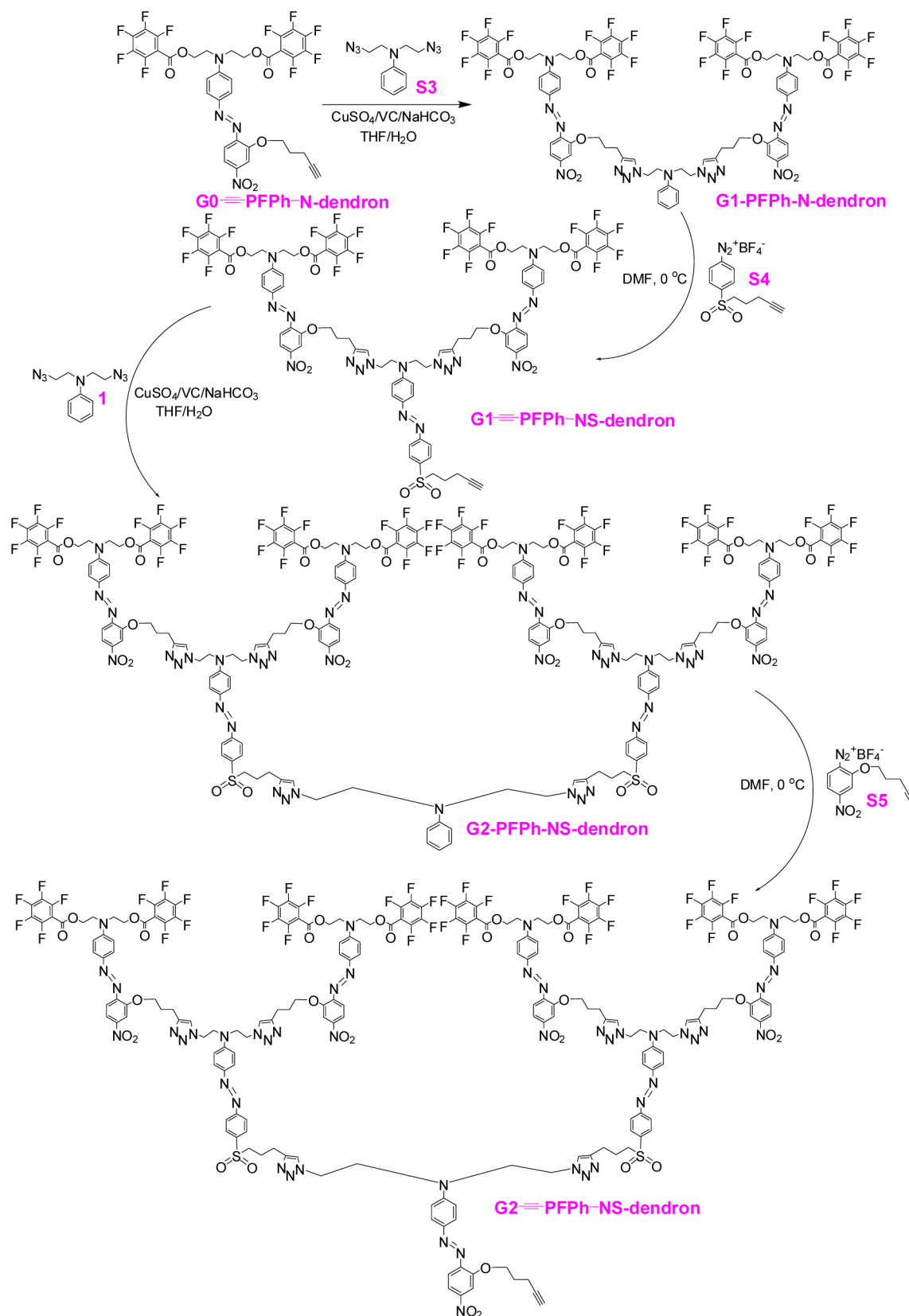


acetate, and then filtered and washed with lots of ethyl acetate and dried in a vacuum at 40°C to a constant weight.

G1-PFPh-NS-GL. **G0-6N₃-S-core** (32.8 mg, 0.02 mmol), **G0-≡PFPh-N-dendron** (112.1 mg, 0.14 mmol). **G1-PFPh-NS-GL** was obtained as red powder (102.4 mg, 79.4%). IR (KBr), ν (cm^{-1}): 1738 (C=O), 1517, 1333 (-NO₂), 1141 (-SO₂-). ¹H NMR (300 MHz, CDCl₃, 298K) δ (TMS, ppm): 2.08 (s, br, -CH₂-), 2.22 (s, br, -CH₂C-), 2.81 (s, br, -CH₂C-), 2.95 (s, br, -CH₂C-), 3.03 (s, br, -CH₂C-), 3.18 (s, br, -SCH₂-), 3.73 (s, br, -NCH₂-), 3.92 (s, br,

-NCH₂-), 4.14 (s, br, -NCH₂-), 4.39 (s, br, -OCH₂-), 4.59 (s, br, -COOCH₂-), 5.41 (s, -NCH₂-), 6.59 (s, br, ArH), 6.85 (s, br, ArH), 7.06 (s, C=CH), 7.59 (m, ArH), 7.77–8.00 (ArH). ¹³C NMR (150 MHz, CDCl₃, 298K) δ (TMS, ppm): 22.0, 22.7, 24.1, 28.6, 29.9, 47.4, 49.9, 51.4, 53.4, 55.5, 63.6, 68.7, 107.6, 109.4, 112.1, 116.7, 117.6, 121.8, 122.6, 123.2, 126.4, 129.2, 137.2, 138.8, 139.0, 144.7, 144.9, 145.3, 146.6, 146.8, 146.9, 147.4, 148.6, 149.6, 150.2, 155.4, 156.0, 159.1. MALDI-TOF MS. Calcd for (C₂₈₂H₂₁₀F₆₀N₆₀O₄₈S₃): m/z [M

Scheme 2. Synthetic Route to the End-Capped Dendrons of Dendrimers



$+\text{Na}^+$: 6466. Found: m/z 6467. $\text{C}_{282}\text{H}_{210}\text{F}_{60}\text{N}_{60}\text{O}_{48}\text{S}_3$ (EA) (%), found/calcd): C, 52.71/52.57; H, 3.59/3.29; N, 13.56/13.04.

G2-PFPPh-NS-GL. **G0-6N₃-N-GL-core** (13.4 mg, 0.008 mmol), **G1-≡PFPPh-NS-dendron** (115.7 mg, 0.056 mmol). **G2-PFPPh-NS-GL** was

obtained as red powder (87.1 mg, 77.6%). IR (KBr), ν (cm^{-1}): 1736 ($\text{C}=\text{O}$), 1516, 1337 ($-\text{NO}_2$), 1142 ($-\text{SO}_2-$). ^1H NMR (300 MHz, $\text{DMSO}-d_6$, 298K), δ (TMS, ppm): 1.7–2.2 ($-\text{CH}_2-$), 2.7–3.0 ($-\text{CH}_2\text{C}-$), 3.6–3.8 ($-\text{NCH}_2-$), 3.8–4.0 ($-\text{NCH}_2-$), 4.1–4.3

($-\text{NCH}_2-$), 4.3–4.6 ($-\text{CH}_2\text{O}-$ and $-\text{CH}_2\text{COO}-$), 5.45 (s, br, $-\text{NCH}_2-$), 6.6–6.8 (ArH), 6.9–7.2 (ArH), 7.4–8.2 (ArH). ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$, 298K) δ (TMS, ppm): 21.2, 22.3, 23.2, 28.2, 42.3, 46.5, 48.8, 49.9, 54.1, 63.6, 68.4, 106.9, 109.2, 112.0, 116.1, 116.9, 122.2, 125.4, 128.8, 135.6, 138.9, 143.2, 144.0, 146.1, 146.6, 147.8, 150.7, 154.7, 158.3. $\text{C}_{618}\text{H}_{477}\text{F}_{120}\text{N}_{141}\text{O}_{105}\text{S}_6$ (EA) (% found/calcd): C, 52.12/52.90; H, 4.00/3.43; N, 13.79/14.08.

G3-PFPh-NS-GL. **G0-6N₃-S-GL-core** (3.06 mg, 0.001865 mmol), **G2-≡PFPh-NS-dendron** (60.0 mg, 0.01306 mmol). **G0-6N₃-S-GL** was obtained as red powder (36.0 mg, 66.1%). IR (KBr), ν (cm^{-1}): 1736 (C=O), 1515, 1337 ($-\text{NO}_2$), 1141 ($-\text{SO}_2-$). ^1H NMR (300 MHz, $\text{DMSO}-d_6$, 298K), δ (TMS, ppm): 1.7–2.2 ($-\text{CH}_2-$), 2.7–3.0 ($-\text{CH}_2\text{C}-$), 3.7–4.0 ($-\text{NCH}_2-$), 4.1–4.2 ($-\text{NCH}_2-$), 4.2–4.6 ($-\text{CH}_2\text{O}-$ and $-\text{CH}_2\text{COO}-$), 5.3–5.5 (s, br, $-\text{NCH}_2-$), 6.5–6.8 (ArH), 6.8–7.0 (ArH), 7.4–8.0 (ArH). $\text{C}_{1290}\text{H}_{1014}\text{F}_{240}\text{N}_{300}\text{O}_{216}\text{S}_{15}$ (EA) (% found/calcd): C, 52.20/53.03; H, 4.00/3.50; N, 13.78/14.38.

Preparation of Polymer 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 dendrimer (Table 4); voltage, 7.5 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.

RESULTS AND DISCUSSION

Synthesis. As shown in Schemes 1 and 2 and Table 1, these dendrimers were conveniently prepared in good yields. The

Table 1. Synthetic Route to Dendrimers G1-PFPh-NS-GL to G3-PFPh-NS-GL

	G0-6N ₃ -N-core	G0-6N ₃ -S-core
G0-≡PFPh-N-dendron		G1-PFPh-NS-GL
G1-≡PFPh-NS-dendron	G2-PFPh-NS-GL	
G2-≡PFPh-NS-dendron		G3-PFPh-NS-GL

“star-type” chromophore cores **G0-6N₃-N-core** or **G0-6N₃-S-core** were prepared through two steps (Scheme 1): the “star-type” chromophore **G0-6Cl-N-core** or **G0-6Cl-S-core** was prepared via the “click chemistry” reaction between the three branched core **S2** and the corresponding chromophore containing two chloroethyl groups and one terminal alkyne group; and then through the substitution of the chloride groups using NaN_3 (N_3^-) as nucleophilic reagent, six azido groups, which could be further modified by “click chemistry”, were introduced to the periphery of the “star-type” chromophore core. On the other hand, in the synthetic route of the convergent approach (Scheme 2), taking the advantage of the combination of click chemistry and azo coupling reaction, **G2-≡PFPh-NS-dendron** could be prepared easily, without any protect/deprotect procedure. At last, the target dendrimers could be yielded by “click chemistry” reaction between the corresponding “star-type” chromophore core and dendrons (Table 1). Because the large different molecular weight between reactants and products, their solubility was different.

Therefore, the purification of these dendrimers was very simple: for example, since **G2-≡PFPh-NS-dendron** and **G1-6N₃-GL-S-core** were easily soluble in ethyl acetate, whereas the product was insoluble, thus, repeating precipitation of its THF solutions into ethyl acetate, **G3-PFPh-NS-GL** could be purified easily. The whole synthetic procedure was very simple and similar to our previous case of other NLO dendrimers, and the obtained dendrimers could be readily soluble in common polar organic solvents, such as THF, DMF, and DMSO, making it convenient to test their NLO and other properties.

Characterizations. The newly prepared dendrimers were well-characterized by spectroscopic methods, such as FT-IR spectra, NMR spectra, and MALDI-TOF MS spectra and so on (for detailed results, see Figures S1–S37 in the Supporting Information). Figure S1 in the Supporting Information was the FT-IR spectra of **G1-PFPh-NS-GL** to **G3-PFPh-NS-GL**, which showed absorption bands associated with the nitro groups at about 1517 and 1338 cm^{-1} and sulfonyl groups at about 1142 cm^{-1} , indicating the success of the introduction of the chromophore moieties into these dendrimers. Also, the peak of azido groups (at about 2100 cm^{-1}) of the azido containing core disappeared in the spectra of high generation dendrimers, and a pentafluorophenyl carbonyl group absorption at 1740 cm^{-1} , derived from the end-capped chromophores, appeared. This disclosed that the target dendrimers were prepared by the “click chemistry” reaction through the “double-stage” approach successfully. This conclusion could be also confirmed by the NMR spectra again. For example, in the ^1H NMR spectra of the target dendrimers **G1-PFPh-NS-GL** to **G3-PFPh-NS-GL**, some characteristic peaks of chromophores and the $-\text{COOCH}_2-$ (about 4.6 ppm) from end-capped groups existed, whereas the peak at about 3.6 ppm, which should be assigned to the protons of the $-\text{CH}_2\text{N}_3$, disappeared.

Considering that there were some perfluorophenyl rings in the periphery of these dendrimers, ^{19}F NMR spectra were also used to confirm the successful synthesis. As shown in Figure 2,

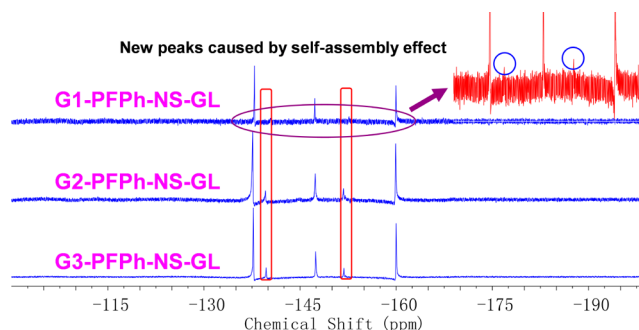


Figure 2. ^{19}F NMR spectra of **G1-PFPh-NS-GL** to **G3-PFPh-NS-GL**.

all of these dendrimers showed three obvious peaks in their ^{19}F NMR spectra, indicating that the end-capped dendrons were linked to the “star-type” chromophore cores via “click chemistry” reaction successfully. However, besides the three original peaks of pentafluorophenyl rings, there were some more peaks appeared in their ^{19}F NMR spectra, indicating the Ar/Ar^F self-assembly effect existed in these dendrimers, because the Ar/Ar^F interaction could change the environment of some F atoms of pentafluorophenyl rings. And from the relative intensity of these new peaks, we could know that the higher generation number, the stronger Ar/Ar^F self-assembly effect,

and their different Ar/Ar^F interactions, caused by their different topological structures.

Gel permeation chromatography (GPC) was usually used to determine the relative molecular weights of macromolecules. Here, the trends in GPC results were consistent with the actual molecular weights: with the increase in the generation number of the dendrimers, the M_w values also increased. And the GPC curves of the dendrimers showed narrow peaks with polydispersity indexes (PDI) less than 1.14, indicating that the products possessed monodispersed molecular weights. However, this GPC analysis using linear polystyrenes as calibration standards often underestimates the molecular weights of dendritic structures with a 3D branched structure, because of their quite different hydrodynamic radii.^{55–57} Therefore, we could use their GPC results to characterize their topological structures: if the difference between the tested value and true one was higher, its hydrodynamic radius should be more different from the linear polymers, and its topological structure might be closer to spherical, which was the most ideal configuration for NLO materials. As shown in Table 2,

Table 2. Some Characterization Data of Dendrimers

	yield (%)	M_w^a	M_w/M_n^a	M_c^b	M_c/M_w	T_g^c (°C)	T_d^d (°C)
G1-PFPh-NS-GL	79.4	5080	1.03	6443	6443	130	222
G2-PFPh-NS-GL	77.6	7240	1.10	14030	14030	136	231
G3-PFPh-NS-GL	66.1	7540	1.14	29214	29214	140	208

^aDetermined by GPC in THF on the basis of a polystyrene calibration. ^b M_c was the calculated molecular weight. ^cGlass transition temperature (T_g) of polymers detected by the DSC analyses under argon at a heating rate of 10 °C/min. ^dThe 5% weight loss temperature of polymers detected by the TGA analyses under nitrogen at a heating rate of 10 °C/min.

accompanying with the generation increase of dendrimers, the difference between the measured and calculated values were increasing, indicating that the globular shape was also improved. Furthermore, the differences in this series of dendrimers were much larger than that of in G1 to G5 (see Table S1 in the Supporting Information), indicating that the topological structure of G1-PFPh-NS-GL to G3-PFPh-NS-GL was more closer to spherical than that of G1 to G5, thanks to the advantages of the “star-type” chromophore core. This better topological structure would be very benefit to the NLO effect.

G1-PFPh-NS-GL to G3-PFPh-NS-GL were thermally stable (see Figure S38 in the Supporting Information), and their temperatures for 5% weight loss are listed in Table 2 (higher than 200 °C). Their degradation temperatures (T_d) were a little lower than those of dendrimers G1 to G5, possibly owing to the presence of the unstable pentafluorophenyl group. However, this result was already sufficient for NLO materials, because the temperature for their application in “real” systems were usually below 200 °C. The glass transition temperature (T_g) of the dendrimers were also investigated by using differential scanning calorimetry (DSC), with the results summarized in Table 2. The growth of new dendrimers resulted in the increased T_g values, similar to our previous case.^{36,37} However, the increase was smaller than before. For example, the T_g value of G3-PFPh-NS-GL was only 10 °C higher than that of G1-PFPh-NS-GL, whereas the T_g value of

G5 was 69 °C higher than G1. In our previous work, we concluded that the increased T_g value should be affected by their topological structure. For example: from G1 to G5, accompanied by the increasing generation number, the topological structure of dendrimers became better and better, and the T_g value also increased to a large degree. Therefore, such small changes between the T_g values of G1-PFPh-NS-GL and G3-PFPh-NS-GL indicated that the topologies of G1-PFPh-NS-GL should already be globular, and suggested that maybe G1-PFPh-NS-GL, a low generation dendrimer, would possess a large NLO effect similar to high generation dendrimers, because of its globular structure. Furthermore, the T_g value of these dendrimers containing pentafluorophenyl were higher than those dendrimers only containing phenyl groups, confirming that the Ar–Ar^F self-assembly effect existed in these dendrimers. The higher T_g value would improve the temporal stability of dipole orientation of chromophore in dendrimers, which would contribute much to practical applications.

It was well-known that to be large macroscopic NLO coefficients usually need NLO chromophore moieties with large dipole moment (μ), which makes the maximum absorption wavelengths (λ_{max}) red-shifted, decreasing the optical transparency of NLO materials. The μ value of sulfonyl-based azo chromophore was smaller than that of nitro-based azo chromophore.⁵⁸ Therefore, the introduction of the sulfonyl-based azo chromophore into these dendrimers could improve their optical transparency. To confirm this point, the UV–vis spectra of G1-PFPh-NS-GL to G3-PFPh-NS-GL in different solvents and films were also tested (Figures 3 and

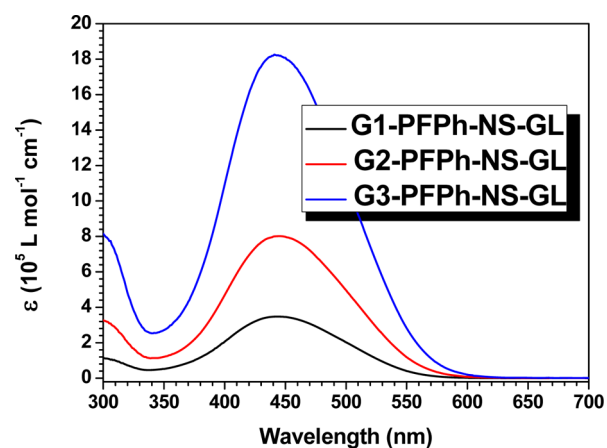


Figure 3. UV–vis spectra of THF solutions of dendrimers (0.02 mg/mL).

Figures S39–S43 in the Supporting Information), and the λ_{max} for the $n-\pi^*$ transition of the azo moieties were listed in Table 3. The molar absorption coefficients (ϵ) of these dendrimers were all very large, because all of them consist of many chromophores. Accompanying with the growth of dendrimers, their ϵ value were enhanced significantly, which was consistent with the enhanced amount of the chromophore: there were 9 chromophores in G1-PFPh-NS-GL (6 nitro-based one and 3 sulfonyl-based one), 21 in G2-PFPh-NS-GL (15 nitro-based one and 6 sulfonyl-based one), and 45 in G3-PFPh-NS-GL (30 nitro-based one and 15 sulfonyl-based one). Furthermore, in comparison with the previous NLO dendrimers only containing nitro-based azo chromophore (for example, G1 to G5, see

Table 3. Maximum Absorption of Dendrimers (λ_{\max} , nm, 0.02 mg/mL)

	THF	1,4-dioxane	chloroform	dichloromethane	DMF	DMSO	film
G1-PFPh-NS-GL	442	435	433	436	455	462	448
G2-PFPh-NS-GL	443	441	438	439	456	465	445
G3-PFPh-NS-GL	441	443	436	436	454	461	444

Table S2 in the Supporting Information), the λ_{\max} of G1-PFPh-NS-GL to G3-PFPh-NS-GL were much blue-shifted in both solutions and films. For example, the λ_{\max} of G3-PFPh-NS-GL was only 444 nm in film, 26 nm more blue-shifted than that of G5, demonstrating much better optical transparency, thanks to the presence of the sulfonyl-based azo chromophore. In addition, different from G1 to G5 (see Table S2 in the Supporting Information), the λ_{\max} values of G1-PFPh-NS-GL, G2-PFPh-NS-GL and G3-PFPh-NS-GL were nearly the same, indicating their topology structures and site-isolation effects were nearly the same.

NLO Properties. As discussed above, it was easily observed the advantages of these three methods of Ar/Ar^F self-assembly, isolation chromophore and “star-type” chromophore. In our previous work on NLO dendritic macromolecules (including dendrimers and hyperbranched polymers), all of these three methods led to higher NLO coefficient. Thus, what would happen when we combined these three methods together? Therefore, we prepared the poled thin films of these dendrimers to evaluate their NLO activity. The most convenient technique to study the second-order NLO activity was to investigate the second harmonic generation (SHG) processes characterized by d_{33} , an SHG coefficient. To check the reproducibility, we repeated the measurements at least three times for each sample. Calculation of the SHG coefficients (d_{33}) for the poled films is based on the following equation

$$\frac{d_{33,s}}{d_{11,q}} = \frac{\chi_s^{(2)}}{\chi_q^{(2)}} = \sqrt{\frac{I_s}{I_q}} \frac{l_{c,q}}{l_s} F$$

where $d_{11,q}$ is d_{11} of the quartz crystals, which is equal to 0.45 pm/V. I_s and I_q are the SHG intensities of the sample and the quartz, respectively, $l_{c,q}$ is the coherent length of the quartz, l_s is the thickness of the polymer film, and F is the correction factor of the apparatus and is equal to 1.2 when l_c is much greater than l_s . From the experimental data, the d_{33} values of these dendrimers were calculated at a fundamental wavelength of 1064 nm (Table 4). Generally, the d_{33} value of the same NLO polymer could be different when measured by different

Table 4. Physical and NLO Results of Dendrimers

	T_e^a (°C)	l_s^b (μm)	d_{33}^c (pm/V)	$d_{33(\infty)}^d$ (pm/V)	Φ^e	N^f
G1-PFPh-NS-GL	120	0.21	221	53	0.25	0.439
G2-PFPh-NS-GL	130	0.22	210	52	0.25	0.442
G3-PFPh-NS-GL	135	0.21	202	51	0.24	0.484

^aThe best poling temperature. ^bFilm thickness. ^cSecond harmonic generation (SHG) coefficient. ^dThe nonresonant d_{33} values calculated by using the approximate two-level model. ^eOrder parameter $\Phi = 1 - A_1/A_0$, A_1 and A_0 are the absorbance of the polymer film after and before corona poling, respectively. ^fThe loading density of the effective chromophore moieties.

methods or different testing systems at different times. To avoid the above-mentioned possible deviations, we tested the NLO properties of all the polymers at the same time.

As shown in Table 4, all of these dendrimers demonstrated large NLO coefficients, and their d_{33} values were all higher than 200 pm/V. However, in comparison with our previous work on NLO dendrimers, the trends of d_{33} values of G1-PFPh-NS-GL to G3-PFPh-NS-GL were much different. We also used G1 to G5 as an example. Accompanying with the increasing generation number, the topological structure of dendrimers became better and better, and the d_{33} value of G5 was also increased to 193.1 pm/V from 100.0 pm/V of G1. Here, the d_{33} values of these three dendrimers were near the same, in the range of 202–221 pm/V. Furthermore, in comparison with other traditional polymer materials with nitro-azobenzene as NLO chromophore (some examples were listed in Figure S44 in the Supporting Information),^{29–35} the d_{33} values of G1-PFPh-NS-GL to G3-PFPh-NS-GL still demonstrated a large advantage. The main reason might be that the topology structure of G1-PFPh-NS-GL was already globular, and the topology structures and site-isolation effects of these three dendrimers were nearly the same as discussed above. As we know, dendrimers, especially high generation dendrimers, were generally prepared expensively as a result of repetitive protection, deprotection, and purification steps. Thus, for the real applications, it was much more difficult to use high generation dendrimers. G1-PFPh-NS-GL was only the first generation dendrimer with the molecular weight of 6443 g/mol, and its synthesis was much easier than those of high generation dendrimers, such as G3-PFPh-NS-GL or G5, making its possible practical applications much cheaper.

Because the films of the dendrimers still had some absorptions at the wavelength of 532 nm (the double frequency of the 1064 nm fundamental wavelength), the NLO properties of dendrimers should be smaller due to the resonant enhancement effect.⁵⁹ Thus, according to the approximate two-level model, their nonresonant d_{33} values could be calculated on the following equation

$$d_{33}/d_{33(\infty)} = \omega_0^4 / [(\omega_0^2 - \omega^2)(\omega_0^2 - 4\omega^2)]$$

where ω_0 was the frequency of the λ_{\max} of dendrimers in film; ω was the frequency of the laser. The results are listed in Table 4. Because of their good optical transparency, as well as their large d_{33} values, their $d_{33(\infty)}$ value were still very high. Also, their d_{33} values were similar, in the range of 51–53 pm/V. To further explore the alignment of the chromophore moieties in these dendrimers, we measured their order parameter (Φ) (Table 4 and Figures S45–S47 in the Supporting Information), which could indicate the alignment of the chromophore moieties under the poling process. Using the equation of $\Phi = 1 - A_1/A_0$, we calculated the Φ values of these dendrimers, with the results listed in Table 2. As expected, their Φ values were very high and nearly the same, confirming our idea again.

Depoling experiments of dendrimers were conducted, in which the real time decays of their SHG signals were monitored as the poled films were heated from 35 to 180 °C in air at a rate

of 4 °C/min. Figure 4 displayed the decay of the SHG coefficient of dendrimers as a function of temperature. Because

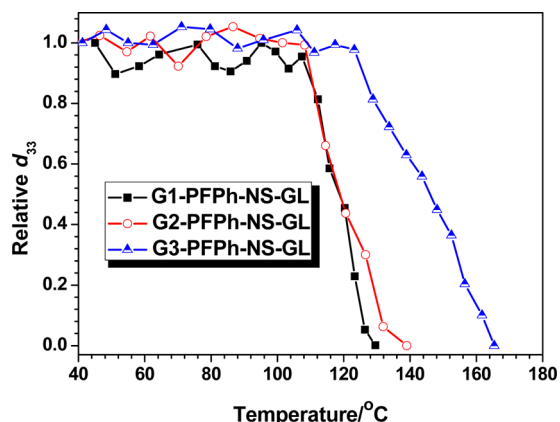


Figure 4. Decay curves of the SHG coefficients of dendrimers G1-PFPh-NS-GL to G3-PFPh-NS-GL as a function of the temperature.

of their higher T_g values caused by the Ar–Ar^F effect, the temporal stability of dipole orientation were also improved. For G3-PFPh-NS-GL, the temperatures for decay in d_{33} value was up to 124 °C, indicating its long-term temporal stability was relatively good, which was good for the practical applications

CONCLUSION

In summary, by the combination of divergent and convergent approach, as well as through the powerful “click chemistry” reaction, a new series of dendrimers G1-PFPh-NS-GL to G3-PFPh-NS-GL were successfully obtained, in which three methods of isolation chromophore, the Ar/Ar^F self-assembly effect and “star-type” chromophore were used to improve their comprehensive performance. All of these dendrimers demonstrated large d_{33} values (higher than 200 pm/V) and excellent optical transparency. Furthermore, the low generation dendrimer G1-PFPh-NS-GL demonstrated similar performance to high generation dendrimer G3-PFPh-NS-GL, which could make the possible practical applications much cheaper.

ASSOCIATED CONTENT

Supporting Information

Some previous NLO dendrimers and polymers, NMR spectra, IR spectra, TOF mass spectra, UV–vis spectra, and TGA thermograms of dendrimers G1-PFPh-NS-GL to G3-PFPh-NS-GL. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: lizhen@whu.edu.cn or lichemlab@163.com. Fax: 86-27-68755363.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to the National Science Foundation of China (21034006), and the National Fundamental Key Research Program (2011CB932702) for financial support.

REFERENCES

- (1) Luo, J.; Huang, S.; Shi, Z.; Polishak, B. M.; Zhou, X.; Jen, A. K. Y. *Chem. Mater.* **2011**, *23*, 544–553.
- (2) Kuzzyk, M. G. *J. Mater. Chem.* **2009**, *19*, 7444–7465.
- (3) Marder, S. R. *Chem. Commun.* **2006**, 131–134.
- (4) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31–75.
- (5) Marder, S. R.; Kippelen, B.; Jen, A. K. Y.; Peyghambarian, N. *Nature* **1997**, *388*, 845–851.
- (6) Lee, M.; Katz, H. E.; Erben, C.; Gill, D. M.; Gopalan, P.; Heber, J. D.; McGee, D. J. *Science* **2002**, *298*, 1401–1403.
- (7) Shi, Y.; Zhang, C.; Zhang, H.; Bechtel, J. H.; Dalton, L. R.; Robinson, B. H.; Steier, W. H. *Science* **2000**, *288*, 119–122.
- (8) Bai, Y.; Song, Z.; Gao, J.; Sun, X.; Wang, X.; Yu, G.; Wang, Z. J. *Am. Chem. Soc.* **2005**, *127*, 2060–2061.
- (9) Dalton, L. R.; Sullivan, P. A.; Bale, D. H. *Chem. Rev.* **2010**, *110*, 25–55.
- (10) Luo, J.; Zhou, X.; Jen, A. K. Y. *J. Mater. Chem.* **2009**, *19*, 7410–7424.
- (11) Robinson, B. H.; Dalton, L. R. *J. Phys. Chem. A* **2000**, *104*, 4785–4795.
- (12) Robinson, B. H.; Dalton, L. R.; Harper, H. W.; Ren, A.; Wang, F.; Zhang, C.; Todorova, G.; Lee, M.; Aniszfeld, R.; Garner, S.; Chen, A.; Steier, W. H.; Houbrecht, S.; Persoons, A.; Ledoux, L.; Zyss, J.; Jen, A. K. Y. *Chem. Phys.* **1999**, *245*, 35–50.
- (13) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665–1688.
- (14) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819–3867.
- (15) Lo, S. C.; Burn, P. L. *Chem. Rev.* **2007**, *107*, 1097–1116.
- (16) Astruc, D.; Boisselier, E.; Ornelas, C. *Chem. Rev.* **2010**, *110*, 1857–1959.
- (17) Mintzer, M. A.; Grinstaff, M. W. *Chem. Soc. Rev.* **2011**, *40*, 173–190.
- (18) Walter, M. V.; Malkoch, M. *Chem. Soc. Rev.* **2012**, *41*, 4593–4609.
- (19) Jang, S.-H.; Luo, J.; Tucker, N. M.; Leclercq, A.; Zojer, E.; Haller, M. A.; Kim, T.-D.; Kang, J.-W.; Firestone, K.; Bale, D.; Lao, D.; Benedict, J. B.; Cohen, D.; Kaminsky, W.; Kahr, B.; Bredas, J.-L.; Reid, P.; Dalton, L. R.; Jen, A. K.-Y. *Chem. Mater.* **2006**, *18*, 2982–2988.
- (20) Marder, S. R.; Cheng, L. T.; Tiemann, B. G.; Friedli, A. C.; Blanchard-Desce, M.; Perry, J. W.; Skindhøj, J. *Science* **1994**, *263*, 511–514.
- (21) Li, Q.; Li, Z.; Zeng, F.; Gong, W.; Li, Z.; Zhu, Z.; Zeng, Q.; Yu, S.; Ye, C.; Qin, J. *J. Phys. Chem. B* **2007**, *111*, 508–514.
- (22) Dalton, L. R.; Steier, W. H.; Robinson, B. H.; Zhang, C.; Ren, A.; Garner, S.; Chen, A.; Londergan, T.; Irwin, L.; Carlson, B.; Fifield, L.; Phelan, G.; Kincaid, C.; Amend, J.; Jen, A. K.-Y. *J. Mater. Chem.* **1999**, *9*, 1905–1920.
- (23) Cho, M. J.; Choia, D. H.; Sullivan, P. A.; Akelaitis, A. J.-P.; Dalton, L. R. *Prog. Polym. Sci.* **2008**, *33*, 1013–1058.
- (24) Pereverzev, Y. V.; Gunnerson, K. N.; Prezhdo, O. V.; Sullivan, P. A.; Liao, Y.; Olbricht, B. C.; Akelaitis, A. J. P.; Jen, A. K.-Y.; Dalton, L. R. *J. Phys. Chem. C* **2008**, *112*, 4355–4363.
- (25) Ma, H.; Liu, S.; Luo, J.; Suresh, S.; Liu, L.; Kang, S. H.; Haller, M.; Sassa, T.; Dalton, L. R.; Jen, A. K.-Y. *Adv. Funct. Mater.* **2002**, *12*, 565–574.
- (26) Shi, Z.; Luo, J.; Huang, S.; Zhou, X.-H.; Kim, T.-D.; Cheng, Y.-J.; Polishak, B. M.; Younkin, T. R.; Block, B. A.; Jen, A. K.-Y. *Chem. Mater.* **2008**, *20*, 6372–6377.
- (27) Luo, J.; Haller, M.; Ma, H.; Liu, S.; Kim, T.-D.; Tian, Y.; Chen, B.; Jang, S.-H.; Dalton, L. R.; Jen, A. K.-Y. *J. Phys. Chem. B* **2004**, *108*, 8523–8530.
- (28) Zhou, X.; Luo, J.; Huang, S.; Kim, T.-D.; Shi, Z.; Cheng, Y.; Jang, S.; Knorr, D. B., Jr.; Overney, R. M.; Jen, A. K.-Y. *Adv. Mater.* **2009**, *21*, 1976–1981.
- (29) Li, Z.; Li, Z.; Di, C.; Zhu, Z.; Li, Q.; Zeng, Q.; Zhang, K.; Liu, Y.; Ye, C.; Qin, J. *Macromolecules* **2006**, *39*, 6951–6961.

- (30) Zeng, Q.; Li, Z.; Li, Z.; Ye, C.; Qin, J.; Tang, B. Z. *Macromolecules* **2007**, *40*, 5634–5637.
- (31) Li, Q.; Li, Z.; Zeng, F.; Gong, W.; Li, Z.; Zhu, Z.; Zeng, Q.; Yu, S.; Ye, C.; Qin, J. *J. Phys. Chem. B* **2007**, *111*, 508–514.
- (32) Li, Z.; Li, P.; Dong, S.; Zhu, Z.; Li, Q.; Zeng, Q.; Li, Z.; Ye, C.; Qin, J. *Polymer* **2007**, *48*, 3650–3657.
- (33) Li, Z.; Dong, S.; Yu, G.; Li, Z.; Liu, Y.; Ye, C.; Qin, J. *Polymer* **2007**, *48*, 5520–5529.
- (34) Li, Z.; Dong, S.; Li, P.; Li, Z.; Ye, C.; Qin, J. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2983–2993.
- (35) Li, Z.; Li, Q.; Qin, J. *Polym. Chem.* **2011**, *2*, 2723–2740.
- (36) Li, Z.; Yu, G.; Wu, W.; Liu, Y.; Ye, C.; Qin, J.; Li, Z. *Macromolecules* **2009**, *42*, 3864–3868.
- (37) Li, Z.; Wu, W.; Li, Q.; Yu, G.; Xiao, L.; Liu, Y.; Ye, C.; Qin, J.; Li, Z. *Angew. Chem., Int. Ed.* **2010**, *49*, 2763–2767.
- (38) Wu, W.; Li, C.; Yu, G.; Liu, Y.; Ye, C.; Qin, J.; Li, Z. *Chem.—Eur. J.* **2012**, *18*, 11019–11028.
- (39) Wu, W.; Ye, C.; Yu, G.; Liu, Y.; Qin, J.; Li, Z. *Chem.—Eur. J.* **2012**, *18*, 4426–4434.
- (40) Wu, W.; Yu, G.; Liu, Y.; Ye, C.; Qin, J.; Li, Z. *Chem.—Eur. J.* **2013**, *19*, 630–641.
- (41) Wu, W.; Huang, L.; Xiao, L.; Huang, Q.; Tang, R.; Ye, C.; Qin, J.; Li, Z. *RSC Adv.* **2012**, *2*, 6520–6526.
- (42) Wu, W.; Huang, Q.; Xu, G.; Wang, C.; Ye, C.; Qin, J.; Li, Z. *J. Mater. Chem. C* **2013**, *1*, 3226–3234.
- (43) Wu, W.; Xin, S.; Xu, Z.; Ye, C.; Qin, J.; Li, Z. *Polym. Chem.* **2013**, *4*, 3196–3203.
- (44) Kim, T. D.; Kang, J.; Luo, J.; Jang, S.; Na, J.; Tucker, N.; Benedict, J. B.; Dalton, L. R.; Gray, T.; Overney, R. M.; Park, D. H.; Herman, W. N.; Jen, A. K. Y. *J. Am. Chem. Soc.* **2007**, *129*, 488–489.
- (45) Zhou, X.; Luo, J.; Huang, S.; Kim, T. D.; Shi, Z.; Cheng, Y.; Jang, S.; Knorr, D. B.; Overney, R. M.; Jen, A. K. Y. *Adv. Mater.* **2009**, *21*, 1976–1981.
- (46) Wu, W.; Huang, Q.; Qiu, G.; Ye, C.; Qin, J.; Li, Z. *J. Mater. Chem.* **2012**, *22*, 18486–18495.
- (47) Wu, W.; Fu, Y.; Wang, C.; Ye, C.; Qin, J.; Li, Z. *Chem. Asian J.* **2011**, *6*, 2787–2795.
- (48) Wu, W.; Qiu, G.; Ye, C.; Qin, J.; Li, Z. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 5124–5133.
- (49) Wu, W.; Wang, C.; Tang, R.; Fu, Y.; Ye, C.; Qin, J.; Li, Z. *J. Mater. Chem. C* **2013**, *1*, 717–728.
- (50) Wu, W.; Huang, L.; Song, C.; Yu, G.; Ye, C.; Liu, Y.; Qin, J.; Li, Q.; Li, Z. *Chem. Sci.* **2012**, *3*, 1256–1261.
- (51) Wu, W.; Wang, C.; Zhong, C.; Ye, C.; Qiu, G.; Qin, J.; Li, Z. *Polym. Chem.* **2013**, *4*, 378–386.
- (52) Gao, J.; Gui, Y.; Yu, J.; Lin, W.; Wang, Z.; Qian, G. *J. Mater. Chem.* **2011**, *21*, 3197–3203.
- (53) Lin, W.; Cui, Y.; Gao, J.; Yu, J.; Liang, T.; Qian, G. *J. Mater. Chem.* **2012**, *22*, 9202–9208.
- (54) Wu, W.; Xu, G.; Li, C.; Qiu, G.; Yu, G.; Liu, Y.; Ye, C.; Qin, J.; Li, Z. *Chem.—Eur. J.* **2013**, *19*, 6874–6888.
- (55) Muchtar, Z.; Schappacher, M.; Deffieux, A. *Macromolecules* **2001**, *34*, 7595–7600.
- (56) Weimer, M. W.; Fréchet, J. M. J.; Gitsov, I. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 955–970.
- (57) Kim, Y.; Webster, O. W. *Macromolecules* **1992**, *25*, 5561–5572.
- (58) Ulman, A.; Willand, C. S.; Kohler, W.; Robello, D. R.; Williams, D. J.; Handley, L. *J. Am. Chem. Soc.* **1990**, *112*, 7083–7090.
- (59) Kauranen, M.; Verbiest, T.; Boutton, C.; Teeren, M. N.; Clays, K.; Schouten, A. J.; Nolte, R. J. M.; Persoons, A. *Science* **1995**, *270*, 966–969.