A Series of Hyperbranched Polytriazoles Containing Perfluoroaromatic Rings from AB₂-Type Monomers: Convenient Syntheses by Click Chemistry under Copper(I) Catalysis and Enhanced Optical Nonlinearity

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On the occasion of the 10th anniversary of click chemistry

Abstract: In this paper, four new hyperbranched polytriazoles containing azo moieties, derived from different AB₂-type monomers, were successfully prepared through the "click" chemistry reaction under copper(I) catalysis by modifying the synthetic route. The polymers were soluble in organic solvents and exhibited good second-order nonlinear optical (NLO) properties. Thanks to the self-assembly of perfluoroaromatic moieties in the periphery, **HP2** showed the best NLO properties, with the d_{33} value as high as 145.0 pm V⁻¹.

Introduction

Due to their unique architectural and functional features, dendritic macromolecules (i.e., dendrimers and hyperbranched polymers) are poised to make significant contributions in several areas of physical and biological science and engineering.^[1,2] Although dendrimers are perfect monodispersed macromolecules with a regular and highly branched three-dimensional architecture, and demonstrate many special properties, including nanometer size, globular shape, multivalent character, and the modularity of the assembly, the syntheses of dendrimers, either in convergent or divergent approaches, are always relatively costly. Alternatively, hyperbranched polymers, with similar unique properties to dendrimers, have attracted much attention in recent years, due to their convenient preparation by a single-step reaction through a one-pot procedure in a large scale and quantity, **Keywords:** click chemistry · copper · hyperbranched polymers · secondorder nonlinear optical effects · self-assembly

regardless of their structural imperfections in comparison with dendrimers.^[2] Fortunately, from AB_2 monomers, but not through the popular A_2+B_3 approach, hyperbranched polymers with the controlled structure more like dendrimers, could be achieved.^[3]

On the other hand, the copper-catalyzed azide-alkyne cycloaddition, also named as the "click chemistry" reaction, has aroused much interest among researchers because of its remarkable features, such as nearly quantitative yields, mild reaction conditions, broad tolerance toward functional groups, low susceptibility to side reactions, and simple product isolation.^[4] As a powerful synthetic tool, this "click" chemistry reaction was successfully applied to the construction of some new functional hyperbranched polymers, with satisfying, even exciting results, generally by taking an A_2+B_3 approach,^[5] in which two monomers containing terminal azido and yne groups were needed. However, related reports were still a little scarce.^[5] As for AB₂ monomers, it was difficult to construct the corresponding soluble hyperbranched polymers through the Cu^I-catalyzed click polymerizations due to self-oligomerization.^[6] Fortunately, by modifying the synthetic procedure and adding the end-capped groups, we have successfully prepared soluble azo-chromophore-containing AB2-type hyperbranched polytriazoles, HP-NO₂ and HP-SO₂ (see Chart S1 in the Supporting Information), which acted as new second-order nonlinear optical (NLO) polymeric materials (one kind of materials with the promise of performance and cost improvements related to telecommunications, computing, embedded network sensing,

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THz wave generation and detection, and many other applications), with very exciting results such as enhanced NLO effects and simple syntheses.^[3a] To pursue the relationship between the structure and properties of this AB₂-type hyperbranched polytriazoles and tackle the challenge in the NLO field (how to efficiently translate the large β values of the organic chromophores into high macroscopic NLO activities of polymers), we have introduced different sizes of the end-capped groups to the periphery of the hyperbranched polymers as isolation moieties to adjust their solubility, processability, and NLO properties (see Chart S2 in the Supporting Information).^[3b] However, with some improvement in their processability and structural adjustment,^[3b] the NLO properties of these hyperbranched polymers were not very satisfying due to the reduced effective concentrations of the chromophore moieties as a result of a large amount of bulky groups in their periphery. Thus, it was required to find some new approaches to improve the processability, solubility, and other properties of the resultant hyperbranched polymers, but without victimizing the possibly enhanced NLO effects.

In 2007, by utilizing the reversible self-assembly of aromatic/perfluoroaromatic dendron-substituted NLO chromophores through the presence of complementary Ar-Ar^F interactions, Jen and co-workers developed a new class of molecular glasses, which exhibited the improved poling efficiency and much enhanced macroscopic NLO effects.^[7] Inspired by their wonderful results, also considering that the properties of the hyperbranched polymers were partially dominated by the nature of their large amounts of end groups in the periphery^[8] and there were no reports concerning the fluoroaromatic moieties containing NLO hyperbranched polymers, we introduced some pentafluorophenyl moieties into the above AB₂-type hyperbranched polytriazoles and investigated their properties. As shown in Scheme 1, the fluorophenyl groups containing four or five fluorine atoms were introduced into the hyperbranched polymers conveniently on the surface of the hyperbranched polymer (HP2), inside (HP3), or both (HP4). For comparison, HP1 without the fluorophenyl moieties was also prepared. Interestingly, the synthetic procedure we reported previously should be modified here at to large degree,^[3] since it was not good enough for the preparation of HP1-HP4. The experimental results demonstrated that the fluorophenyl moieties in the polymers played an important role in their properties. For example, with pentafluorophenyl moieties as end groups in the periphery, HP2 exhibited about 24% higher macroscopic NLO performance than that of HP1, no matter if the effective concentration of the chromophore moieties in HP2 was reduced to about 15%. Similar phenomena were observed in the case of HP3 and HP4. Furthermore, relative to HP-NO₂ and HP-SO₂, the processability of HP1-HP4 was much improved. Herein, we would like to present the syntheses, characterization, and properties of these hyperbranched polymers in detail.

Results and Discussion

Synthesis

The overall pathway of monomer M2 and the end-capped chromophore C2 was given in Scheme 2, whereas monomer M1 and the end-capped chromophore C1 were prepared previously.^[9] As shown in Scheme 2, compound **S3** was prepared through the esterification reaction between N-phenyldiethanol (S1) and pentafluorobenzoic acid (S2) under mild conditions. As different fluorine atoms possessed different activities in the pentafluorophenyl group in S3, compound S4 could be prepared through a nucleophilic substitution reaction by using NaN_3 (N_3^-) as the nucleophilic reagent while other fluorine atoms were not involved in the reaction. Then, under the normal azo coupling reaction conditions, especially at the low reaction temperature (0°C), monomer M2 and the end-capped chromophore C2 could be obtained in satisfactory yields. Similar to those in M1, both of the azido and yne groups were present in M2. Once the temperature was a little higher than room temperature, these two active groups could react with each other as a result of their high reactivity. That was to say, if the reaction temperature was a little higher, perhaps, this monomer could not be obtained. Fortunately, according to our previous work of preparing M1,^[3a] we used the azo coupling reaction at 0°C to avoid the cycloaddition reactions at this stage. The pure monomer M2 was stable during its storage in the refrigerator for about one year.

As mentioned in the Introduction, in some special cases, the Cu¹-catalyzed click polymerizations of the AB₂ monomers failed to yield soluble hyperbranched polymers, due to self-oligomerization.^[6] Thus, the polymerization process of the above monomers, M1 and M2, should be handled very carefully. Previously, we found that AB2-type polytriazoles could be successfully prepared by adjusting the synthetic procedure of the click reaction from monomer M1 through two stages: at the first stage of the polymerization process, the hyperbranched polymeric intermediate HP-N₃ (see Chart S3 in the Supporting Information), which possessed a large amount of unreacted azido groups in the periphery, was synthesized; then, at the second stage, the end-capped group and another batch of catalysts were added into the reaction solution of HP-N₃ to react with the peripheric azido groups in **HP-N₃**.^[3] As shown in Scheme 1, the hyperbranched polytriazoles HP1-HP4 were prepared from the same monomer or similar monomer to that used previously,^[3] thus they should be prepared according to the previous procedure. However, in the polymerization process, as the activities of the azido groups of the two monomers were different, the actual polymerization conditions were different, that is, the amounts of catalysts used to prepare HP3 and HP4 were not identical to those for HP1 and HP2. The specific reaction times and amounts of catalysts are presented in Table 1 and the Experimental Section. The longer reaction time and more catalysts needed disclosed the relatively poor activity of the azido groups in monomer M2. This was

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Scheme 1. Synthesis of NLO hyperbranched polymers. $DMF = N_{,N}$ -dimethylformamide.

reasonable, since the azido group was bonded to the aromatic ring, unlike that linked with alkyl moieties in **M1**.

Structural Characterization

The overall synthetic route was simple and efficient, in which different chromophore moieties and functional endcapped groups could be easily introduced. Thus, these results confirmed the reproducibility, reliability, and extensity of the controllable synthetic process for the hyperbranched polymers from AB_2 monomers through the Cu¹-catalyzed click polymerization by modifying the synthetic procedure and using end-capped groups once again. It was believed that many other AB_2 -type hyperbranched polymers could be obtained, inspired by our preliminary results. The monomers and polymers were characterized by spectroscopic methods, and all gave satisfactory spectral data (see Figures S1–S19 in the Supporting Information). Compounds S3, S4, monomer M2, and the end-capped chromophore C2 were new compounds. From the ¹H NMR and mass spectra, the structure of S3 was confirmed by NMR spectroscopy, mass spectroscopy, and elemental analyses. The structure of S4 was similar to S3, thus the ¹H (Figure 1) and ¹³C NMR spectra just produced a little change. For example, the chemical shift of methylene groups bonding to the oxygen



Scheme 2. Synthesis of monomer M2 and end-capped chromophore C2. EDC = 3-(ethyliminomethyleneamino)-N,N-dimethyl-propan-1-amine, DMAP = 4-dimethylaminopyridine.

Table 1. Some related data of polymerizations.

Compound no.	$t_1 [h]^{[a]}$	$t_2 [h]^{[b]}$	$n_1 [\%]^{[c]}$	$n_2 [\%]^{[d]}$	Yield [%]	
HP1	16	12	10	3.3	88.7	
HP2	16	12	10	3.3	72.6	
HP3	24	24	10	5	58.9	
HP4	24	24	10	5	60.2	

[a] Polymerization time before the addition of the end-capped chromophore. [b] Reaction time after the addition of the end-capped chromophore. [c] Amount of catalyst before the addition of the end-capped chromophore. [d] Amount of catalyst after the addition of the end-capped chromophore.

Figure S20 (Supporting Information) showed the IR spectra of **HP1–HP4**, the absorption bands associated with the nitro groups were at about 1520 and 1340 cm^{-1} . However, it was easily seen that there was a weak absorption at about



Figure 1. 1 H NMR spectra of **S3** and **S4** conducted in [D]chloroform. The solvent peaks are marked with asterisks (*).

atom of **S4** was $\delta = 4.53$ ppm, whereas that of **S3** was at $\delta = 4.54$ ppm. To further confirm the structure of **S4**, ¹⁹F NMR spectroscopy was conducted. As shown in Figure 2, one peak in the ¹⁹F NMR spectra of **S4** disappeared in comparison with **S3**, coupled with the appearance of an absorption band at about 2095 cm⁻¹ ($-N_3$) in the IR spectra (Figure 3), the results verified that the reaction proceeded successfully. Similar to this, the structures of monomer **M2** and end-capped chromophore **C2** were confirmed (see Figures S5–S10 in the Supporting Information).



 2100 cm^{-1} in their spectra, which indicated that there were still some azido groups that remained unreacted. Relative to the corresponding absorption of the monomers and the absorption at about 1740 cm⁻¹ (C=O) in the same spectrum, which was the absorption of the carbonyl of the end-capped chromophore, the absorption bands of the azido groups were very weak, disclosing that the amount of azido groups was small. Actually, in the polymerization procedure, the whole process of the click reaction was monitored by IR spectroscopy, and only when the absorption peak of the azido group at about 2095 cm⁻¹ disappeared was the reaction was terminated. That is to say, during the synthesis of the hyperbranched polymers, no peak of the azido groups



Figure 3. FTIR spectra of S3, S4, and monomer M2.

was observed in the IR spectrum of the reaction mixture when the reaction was stopped. However, the weak absorption of the azido groups was observed in the IR spectra. This should be caused by the low concentration of azido groups in the reaction mixture when monitored. Fortunately, although the hyperbranched polymers contained some unreacted azido groups, they were very stable during the storage and characterization process, which indicated that a small amount of azido moieties would not lead to cross-linking of the hyperbranched polymers. The reason for this might be that the azido moieties were surrounded by other bulky groups in the polymers. In fact, we also prepared a similar hyperbranched polymer, HP5, without end-capped groups (see Scheme S1 in the Supporting Information). As expected, it could not dissolve in any solvent after about one week, whereas HP1-HP4 still maintained a good solubility after 12 months.

In all the ¹H NMR spectra of the polymers, the chemical shifts were consistent with the polymer structures demonstrated in Scheme 2 (see Figures S11-S19 in the Supporting Information). From their ¹H NMR spectra, it was easy to confirm the success of the polymerization by using a click reaction. For example, in the ¹H NMR spectra, there was a separate peak observed at $\delta = 2.8-3.1$ ppm, which should be ascribed to the methylene groups bonded to the carbon atom of the newly formed triazole rings, whereas in the ¹H NMR spectrum of M2, those methylene groups bonded to terminal alkyne moieties appeared at about $\delta = 2.5$ ppm. Also, a new peak at $\delta = 4.5$ ppm appeared in **HP1** and **HP2**, which should be assigned to the methylene groups linked to the nitrogen atom of the newly formed triazole rings and the methylene groups bonded to the oxygen atom of the end-capped chromophore. However, this phenomenon was not apparent in the ¹H NMR spectra of HP3 and HP4, because monomer M2 has the peak at the same chemical shift assigned to the methylene groups bonded to the oxygen atom in the ¹H NMR spectrum. However, from their ¹⁹F NMR spectra, the success of the end-capping reaction by

using the click chemistry reaction was clear. For example, there was no peak in the ¹⁹F NMR spectra of HP1 and its corresponding monomer (see Figure S13 in the Supporting Information), but there were three peaks in the ¹⁹F NMR spectra of HP2 (see Figure S15 in the Supporting Information), which should be ascribed to the pentafluorophenyl end-capped chromophore. Interestingly, some more peaks appeared in the ¹⁹F NMR spectra of HP3 (see Figure S17 in the Supporting Information), than its corresponding monomer M2 (see Figure S10 in the Supporting Information). This should be ascribed to the different chemical environment of the internal fluorophenyl moieties, which might indicate the possible presence of the self-assembly of perfluoroaromatic moieties inside the hyperbranched polymer of HP3. Similar phenomena were observed in the case of HP4 (see Figure S19 in the Supporting Information). To obtain more information, some control experiments were conducted: the ¹⁹F NMR spectra of different mixtures, including C1 and M2, C2 and M1, C2 and M2, and HP1 and HP2 were measured. No additional peaks appeared in the ¹⁹F NMR spectra (see Figures S21-S27 in the Supporting Information), disclosing another possibility that the actual interaction between the fluorophenyl group and the phenyl one was totally different in the hyperbranched structure from those in the physical mixtures, which indicated the special properties of the dendritic structure.

The molecular weights of **HP1–HP4** were determined by gel-permeation chromatography (GPC) with THF as an eluent and polystyrene standards as calibration standards. As shown in the Experimental Section, these four hyperbranched polymers possessed high molecular weights. Thus, the polymerization method reported here was successful to construct hyperbranched polymeric structures with high molecular weights and good solubility from AB_2 monomers through the click reaction. The polymers were thermally stable, as shown in Figure 4, with the 5% weight loss temperature of polymers listed in Table 2. Here, **HP1** exhibited the best thermal stability and **HP4** the worst. The reason for this might be that the pentafluorophenyl group was not so



Figure 4. TGA thermograms of **HP1–HP4** measured in nitrogen at a heating rate of 10° Cmin⁻¹.

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Table 2. Characterization data of polymers.

Compd.no.	$T_{\rm g} \\ [^{\rm o}{\rm C}]^{[\rm a]}$	T_{d} [°C] ^[b]	T_{e} [°C] ^[c]	<i>l</i> s [μm] ^[d]	d_{33} [pm V ⁻¹] ^[e]	$d_{33(\infty)} \ [m pm V^{-1}]^{[f]}$	$arPsi^{[\mathrm{g}]}$	$N^{[h]}$
HP1		276	145	0.24	116.8	20.9	0.21	0.55
HP2		244	148	0.26	145.0	25.9	0.23	0.47
HP3	155	217	178	0.21	104.7	18.7	0.18	0.41
HP4	162	178	170	0.18	121.7	21.8	0.22	0.36

[a] Glass transition temperature (T_g) of polymers detected by the DSC analyses under nitrogen at a heating rate of 10 °Cmin⁻¹. [b] The 5% weight loss temperature of polymers detected by the TGA analyses under nitrogen at a heating rate of 10 °Cmin⁻¹. [c] The best poling temperature. [d] Film thickness. [e] Second harmonic generation (SHG) coefficient. [f] The nonresonant d_{33} values calculated by using the approximate two-level model. [g] Order parameter $\Phi = 1 A_1 A_{-10}^{-1}$, A_1 and A_0 are the absorbance of the polymer film after and before corona poling, respectively. [h] The loading density of the effective chromophore moieties.

stable. The glass transition temperatures (T_g) of the polymers were also investigated by using a differential scanning calorimeter (DSC) with the results summarized in Table 1. **HP3** and **HP4** exhibited a high T_g values of 155 and 162 °C, respectively.

All the hyperbranched polymers were soluble in common polar organic solvents, such as THF, DMF, and DMSO. Their solutions could be easily spin-coated into thin solid films; therefore, it was convenient to test their NLO properties based on the thin films. The UV/Vis absorption spectra of the chromophores and polymers in different solvents were demonstrated in Figure 5 and Figures S28-S32 in the Supporting Information, with the maximum absorption wavelengths for the π - π * transition of the azo moieties in them listed in Table S1 (Supporting Information). Figure 5 demonstrated the UV/Vis spectra of the hyperbranched polymers in chloroform, and all the polymers exhibited blue-shifted maximum absorption wavelength in comparison with HP-NO₂. Our previous work has demonstrated that the [1,2,3]-triazole rings surrounding the chromophore moieties could act as good isolation moieties, leading to the effective



Figure 5. UV/Vis spectra of polymers in chloroform (0.02 mg mL $^{-1}$).

site-isolation effect.^[3,10] Here, similar results were obtained, and the better effective site-isolation effect could be achieved in HP1-HP4 rather than in HP-NO₂. This should be due to the different isolated groups (phenyl or pentafluorophenyl) of the end-capped chromophore moieties, which nearly constructed the primary interface between the hyperbranched polymers and the environment. The results were similar to our previous work. However, HP3 and HP4 demonstrated nearly the same maximum absorption wavelength to HP1 and HP2, despite the fact that they have different isolated groups. This meant that the size of [1,2,3]-triazole rings should be big enough for them to be used as good isolation moieties surrounding the chromophore moieties and the superfluous pentafluorophenyl in the interior architecture of hyperbranched polymers could not make the effective site-isolation effect better.

NLO Properties

To evaluate the NLO activity of the polymers, their poled thin films were prepared. In our previous work, **HP-NO**₂ exhibited bad processability, and it could not form high-quality thin films through spin-coating.^[3a] In this work, we used the chromophores with isolated groups as end-capped moieties to prepare the polymers and improve their processability: all the polymers could easily form high-quality thin films through spin-coating.

The 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. The method for the calculation of the SHG coefficients (d_{33}) for the poled films has been reported previously.^[11] From the experimental data, the d_{33} values of polymers were calculated at 1064 nm fundamental wavelength. To check the reproducibility, we repeated the measurements three times and nearly got the same results. As shown in Table 2, the d_{33} values of the polymers with the pentafluorophenyl groups as the isolated groups in the periphery, HP2 and HP4, were higher than their corresponding polymers with phenyl as the isolated moieties, HP1 and HP3; this was reasonable. As mentioned in the Introduction, many previous literature reports have reported that there were strong intermolecular interactions between aromatic rings and perfluoroaromatic rings. Here, in comparison with HP1 or HP3, there were many pentafluorophenyl groups in the periphery of HP2 and HP4. The role of self-assembly between that pentafluorophenyl and phenyl groups would make the pentafluorophenyl the perfect interface between the chromophores in the interior architecture and environment. That is to say, pentafluorophenyl groups, which are attached to the surface of hyperbranched polymers, would be a good isolated interface between two molecules and greatly reduce the intermolecular dipole-dipole interactions between chromophores. Also, just as reported by Jen et al.^[7] the complementary Ar-Ar^F interactions could improve the poling efficiency of the materials, leading to the enhanced d_{33} values. However, the perfluoroaromatic rings in the interior architecture

didn't result in higher d_{33} values, because in the interior architecture, perfluoroaromatic rings were fixed between two chromophore moieties; this special structure reduced the intermolecular interactions between perfluoroaromatic and aromatic rings and made the perfluoroaromatic rings in the interior architecture more like normal isolated groups; however, it might be too large. The large bulk of the pentafluorophenyl moieties meant the low loading density of the effective chromophore moieties. It was well-known that in theory, under identical experimental conditions, the d_{33} value was proportional to the density of the chromophore moieties. So the d_{33} values of HP3 and HP4 were lower than HP1 and HP2, as a result of the lower density of the chromophore moieties. However, due to their outstanding siteisolation effects and the presence of complementary Ar-Ar^F interactions in some degree, the d_{33} values of HP3 and HP4 were much higher than other hyperbranched polymers, which possessed similar structure and density to the chromophore moieties. For example, the d_{33} value of HP4 $(121.7 \text{ pm V}^{-1})$ was nearly two times that of **P6** (63.7 pm V⁻¹; see Chart S1 in the Supporting Information),^[3b] although they possessed the same density of the chromophore moieties and similar chemical structure.

As there might be some resonant enhancement due to the absorption of the chromophore moieties at 532 nm, the NLO properties of HP1-HP4 should be much smaller as shown in Table 2 $(d_{33}(\infty))$, which were calculated by using the approximate two-level model. Due to their relatively good optical transparency, these hyperbranched polymers exhibited good $d_{33}(\infty)$ values, with that of **HP1** as high as 20.9 pm V^{-1} . Also, HP2 and HP4 demonstrated satisfactory $d_{33}(\infty)$ values due to the pentafluorophenyl groups in the periphery. To further explore the alignment of the chromophore moieties in the polymers, we measured their order parameter (ϕ). Figures S33–S36 in the Supporting Information show the UV/Vis spectra of the films of HP1-HP4 before and after corona poling. It was easily seen that after the corona poling, the dipole moments of the chromophore moieties in the polymers were aligned and the absorption curves decreased due to birefringence. From the absorption change, the Φ values for the polymers could be calculated according to the equation presented in Table 2 (see footnote [g]), and **HP2** exhibited the highest value.

The dynamic thermal stabilities of the NLO activities of **HP1–HP4** were investigated by the depoling experiments, in which the real time decays of their SHG signals were monitored as the poled films were heated from room temperature to 160 °C in air at a rate of 4 °Cmin⁻¹. Figure 6 showed the decay of the SHG coefficient of **HP1–HP4** as a function of temperature: as the chemical structure of them was similar, the onset temperatures for decays of them all was around 105 °C, higher than **HP-NO₂** (93 °C). The results indicated that the long-term temporal stability of the hyperbranched polymers was relatively good.



Figure 6. Decay curves of the SHG coefficients of hyperbranched polymers HP1-HP4 as a function of the temperature (\blacksquare : HP1, \bullet : HP2, \blacktriangle : HP3, \bullet : HP4).

Conclusions

In summary, four new azo chromophore containing hyperbranched polytriazoles, HP1-HP4, derived from different AB₂ monomers and bearing different end-capped chromophores, were successfully prepared by click chemistry under copper(I) catalysis by modifying the synthetic procedure. All the polymers exhibited higher macroscopic NLO effects, in comparison with other hyperbranched polytriazoles with the similar structure and loading density of the effective chromophore moieties, thanks to the additional complementary Ar-Ar^F interactions. Different chemical structures led to different effects: the pentafluorophenyl in the periphery produced higher d_{33} values than the normal phenyl in the periphery, whereas the perfluoroaromatic rings in the interior architecture produced slightly lower d_{33} values due to the lower loading density of the effective chromophore moieties. Compound HP2 with pentafluorophenyl in the periphery and acceptable loading density of the effective chromophore moieties has the highest d_{33} values (145.0 pm V⁻¹). Thus, the introduction of the pentafluorophenyl groups into the periphery of hyperbranched polymer should be a new approach to enhance the macroscopic NLO effects of polymers.

Experimental Section

Materials

THF was dried over and distilled from K/Na alloy under an atmosphere of dry nitrogen. Dichloromethane (CH_2Cl_2) was dried over CaH_2 and distilled under normal pressure before use. DMF was dried over CaH_2 and distilled under reduced pressure before use. Chromophores **C1** and **M1** were synthesized previously.^[9] Pentafluorobenzoic acid (**S2**) was purchased from Alfa-Aesar. All other reagents were used as received.

Instrumentation

¹H and ¹³C NMR spectra were measured on a Varian Mercury300 spectrometer by using tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard. ¹⁹F NMR spectra were measured on a Varian Mercury600 spectrometer. FTIR spectra were recorded on a Perkin–Elmer-2 spectrometer

in the region of 3000–400 cm⁻¹ on KBr pellets. UV/Vis spectra were obtained by using a Shimadzu UV-2550 spectrometer. Elemental analyses were performed by a CARLOERBA-1106 microelemental analyzer. GPC was used to determine the molecular weights of polymers. GPC analysis was performed on a Waters HPLC system equipped with a 2690D separation module and a 2410 refractive index detector. Polystyrene standards were used as calibration standards for GPC, THF was used as an eluent, and the flow rate was 1.0 mLmin⁻¹. Thermal analysis was performed on a NETZSCH STA449C thermal analyzer at a heating rate of 10 °Cmin⁻¹ in nitrogen at a flow rate of 50 cm³min⁻¹ for thermogravimetric analysis (TGA) and the thermal transitions of the polymers. The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

Synthesis of S3

N-Phenyldiethanolamine (S1) (1.08 g, 6.0 mmol), pentafluorobenzoic acid (S2) (3.18 g, 15.0 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (5.75 g, 30.0 mmol), and 4-(N,N-dimethyl)aminopyridine (DMAP) (288 mg, 2.40 mmol) were dissolved in dry CH₂Cl₂ (120 mL) and stirred at room temperature for 3 h and then treated with a saturated solution of citric acid and extracted with CH2Cl2. The resulting mixture was washed with brine and a saturated solution of citric acid. After removal the organic solvent, the crude product was purified by column chromatography on silica gel by using chloroform/petroleum ether (1:1, v/v) as the eluent to afford a white solid (2.92 g, 84.2%). IR (KBr): $\tilde{v} = 1732 \text{ cm}^{-1}$ (C=O); ¹H NMR (300 MHz, CDCl₃, 298 K): δ (TMS)=3.79 (t, J=6.0 Hz, 4H; $-NCH_2-$), 4.54 (t, J=6.0 Hz, 4H; -OCH₂-), 6.78 (d, J=7.8 Hz, 2 H; ArH), 7.26 ppm (m, 3 H; ArH); ¹³C NMR (75 MHz, CDCl₃, 298 K): $\delta = 49.5$, 63.6, 112.1, 117.3, 129.4, 146.5, 158.9 ppm; $^{19}{\rm F}\,{\rm NMR}\,$ (564 MHz, CDCl₃, 298 K): $\delta\!=\!-138.32\,$ (d, J=1.69 Hz), -148.20 (t, J=2.04 Hz), -160.50 ppm (t, J=1.86 Hz); MS (EI): m/z: calcd: 569.07 [M^+]; found: 569.07; elemental analysis calcd (%) for $C_{24}H_{13}NO_4F_{10}$: C 50.85, H 2.62, N 2.34; found: C 50.63, 6.30, 2.46.

Synthesis of S4

Compound S3 (1.14 g, 2.0 mmol) and NaN₃ (260 mg, 8.0 mmol) were dissolved in dry DMF (20 mL) and stirred at 80 °C for 12 h under an atmosphere of argon. Then, the reaction mixture was treated with distilled water, extracted with CH₂Cl₂, 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 by using chloroform/petroleum ether (1:1, v/v) as the eluent to afford a pale-yellow solid (1.17 g, 95.0%). IR (KBr): $\tilde{\nu} = 2125$ (-N₃), 1728 cm⁻¹ (C=O); ¹H NMR (300 MHz, CDCl₃, 298 K): δ (TMS) = 3.80 (t, J = 6.0 Hz, 4H; -NCH₂-), 4.53 (t, J = 6.0 Hz, 4H; -OCH₂-), 6.78 (d, J =8.1 Hz, 2H; ArH), 7.26 ppm (m, 3H; ArH); ¹³C NMR (75 MHz, CDCl₃, 298 K): $\delta = 49.5$, 63.5, 112.1, 117.4, 129.4, 146.5, 159.1 ppm; ¹⁹F NMR (564 MHz, CDCl₃, 298 K): $\delta = -138.82$ (d, J = 0.68 Hz), -151.17 ppm; MS (EI): m/z: calcd: 615.03 [M⁺]; found: 615.09; elemental analysis calcd (%) for $C_{24}H_{13}N_7O_4F_8$: C 46.71, H 2.18, N 15.83; found: C 46.84, H 2.13, N 15.93.

General Procedure for the Synthesis of Chromophores C2 and M2

Compound **S3** or **S4** and diazonium salt with equal equivalents were dissolved in DMF at 0 °C. The reaction mixture was stirred for 12 h at 0 °C and then treated with H_2O and extracted with CH_2Cl_2 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.

Chromophore C2

Compound **S3** (569 mg, 1.00 mmol), diazonium salt (**S5**) (319 mg, 1.00 mmol). The crude product was purified by column chromatography on silica gel by using ethyl acetate/petroleum ether (1:4,v/v) as the eluent to afford a deep-red solid (644 mg, 80.4%). ¹H NMR (300 MHz, CDCl₃, 298 K): δ (TMS)=2.01 (s, 1H; $-C \equiv CH$), 2,15 (m, 2H; $-CH_2-$), 2.51 (m, 2H; $-CH_2C-$), 3.94 (t, J = 5.4 Hz, 4H; $-NCH_2-$), 4.36 (t, J = 5.7 Hz, 2H;

−OCH₂−), 4.62 (t, *J*=5.4 Hz, 4H; −OCOCH₂−), 6.87 (d, *J*=8.7 Hz, 2H; ArH), 7.67 (d, *J*=8.7 Hz, 1H; ArH), 7.93 ppm (m, 4H; ArH); ¹³C NMR (75 MHz, CDCl₃, 298 K): δ =15.0, 27.9, 49.5, 63.3, 68.0, 69.1, 83.1, 109.1, 111.7, 116.4, 117.3, 126.0, 139.4, 141.7, 145.0, 146.6, 148.4, 149.9, 155.2, 158.8 ppm; ¹⁹F NMR (564 MHz, CDCl₃, 298 K): δ =−138.16 (d, *J*= 1.69 Hz), −147.56 (t, *J*=2.04 Hz), −160.19 ppm (t, *J*=2.04 Hz); MS (EI): *m/z*: calcd: 800.13 [*M*⁺]; found: 800.19; elemental analysis calcd (%) for C₃₅H₂₂N₄O₇F₁₀: C 52.87, H 2.92, N 6.89; found: C 52.51, H 2.77, N 7.00; UV/Vis (THF, 1×10⁻⁵ mmolmL⁻¹): λ_{max} =459 nm.

Chromophore M2

Compound **S4** (615 mg, 1.00 mmol), diazonium salt (**S5**) (319 mg, 1.00 mmol). The crude product was purified by column chromatography on silica gel by using ethyl acetate/petroleum ether (1:4, v/v) as the eluent to afford a deep-red solid (534 mg, 63.1 %). IR (KBr): \bar{v} =3307 (C=C-H), 2129 (-N₃), 1731 (C=O), 1516, 1334 cm⁻¹ (-NO₂); ¹H NMR (300 MHz, CDCl₃, 298 K): δ (TMS)=2.01 (s, 1H; -C=CH), 2,15 (m, 2H; $-CH_2$ -), 2.51 (m, 2H, $-CH_2$ C-), 3.93 (brs, 4H; $-NCH_2$ -), 4.36 (t, J=5.7 Hz, 2H; $-OCH_2$ -), 4.60 (brs, 4H; $-OCOCH_2$ -), 6.87 (d, J= 8.7 Hz, 2H; -AH), 7.67 (d, J=8.7 Hz, 1H; ArH), 7.93 ppm (m, 4H; ArH); ¹³C NMR (75 MHz, CDCl₃, 298 K): δ =15.0, 27.9, 49.5, 63.1, 68.0, 69.1, 83.1, 109.1, 111.7, 116.4, 117.3, 126.0, 138.6, 141.9, 145.0, 146.6, 148.4, 150.0 155.2, 159.1 ppm; ¹⁹F NMR (564 MHz, CDCl₃, 298 K): δ =-138.69 (d, J=1.24 Hz), -150.98 ppm (d, J=1.24 Hz); elemental analysis calcd (%) for C₃₅H₂₂N₁₀O₇F₈: C 49.9, H 2.91, N 17.01; found: C 49.65, H 2.62, N 16.54; UV/Vis (THF, 1×10⁻⁵ mmol mL⁻¹): λ_{max} =461 nm.

General Procedure for the Synthesis of Hyperbranched Polymers HP1– HP4

The hyperbranched polymers were synthesized by Cu-catalyzed cycloadditions from different monomers **M1** or **M2** and different end-capped chromophores **C1** or **C2**, respectively. A typical experimental procedure for the preparation of **HP1** is given below as an example.

Preparation of HP1

Chromophore M1 (69.4 mg, 0.15 mmol) was dissolved in DMF (7.5 mL) under nitrogen. Then aqueous solutions of CuSO4 (187.5 µL, 0.04 M) and NaAsc (187.5 µL, 0.08 м) were dropped into the solution, respectively. After the reaction had been stirred for 16 h at room temperature, the end-capped chromophore C1 (111.7 mg, 0.18 mmol) was added and, at the same time, another batch of CuSO₄ (62.5 µL, 0.04 M) and NaAsc (62.5 µL, 0.08 M) was also added. The reaction mixture left to stir for 12 h. After this time, a lot of water was poured into the mixture, which was then filtered and washed with methanol and acetone. The obtained solid was further purified by reprecipitation from its THF solution into methanol to afford red powder **HP1** (144.1 mg, 88.7 %). $M_{\rm w} = 6.04 \times 10^4$, $M_{\rm w}/M_{\rm n}$ =2.19 (GPC, polystyrene calibration); IR (thin film): $\tilde{\nu}$ =2098 $(-N_3)$, 1716 (C=O), 1516, 1338 cm⁻¹ (-NO₂); ¹H NMR (300 MHz, $[D_6]$ DMSO, 298 K): $\delta = 1.6-2.1$ (-CH₂-), 2.6-2.8 (-CH₂-), 3.6-4.2 (-N-CH2-), 4.2-4.6 (-O-CH2-), 6.6-6.8 (ArH), 6.9-7.1 (ArH), 7.2-8.0 ppm (ArH); 13 C NMR (75 MHz, [D₆]DMSO, 298 K): $\delta = 21.9, 29.0, 47.3, 49.6,$ 51.7, 62.7, 68.4, 69.0, 79.6, 112.7, 117.5, 119.0, 123.3, 126.2, 127.9, 129.1, 129.7, 133.9, 144.7, 146.8, 155.3, 166.3 ppm; UV/Vis (THF, 0.02 mg mL⁻¹): $\lambda_{\rm max} = 464$ nm.

Preparation of HP2

Chromophore **M1** (69.4 mg, 0.15 mmol), **C2** (144.1 mg, 0.18 mmol). After the reaction had been stirred for 16 h, the end-capped chromophore **C2** was added for the next 12 h reaction. Red powder (137.5 mg, 72.6%); M_w =10.97×10⁴, M_w/M_n =2.01 (GPC, polystyrene calibration); IR (thin film): $\tilde{\nu}$ =2101 (-N₃), 1737 (C=O), 1516, 1339 cm⁻¹ (-NO₂); ¹H NMR (300 MHz, [D₆]DMSO, 298 K): δ =1.7-2.2 (-CH₂-), 2.7-2.9 (-CH₂-), 3.6-4.2 (-N-CH₂-), 4.2-4.6 (-O-CH₂-), 6.6-6.8 (ArH), 6.9-7.1 (ArH), 7.2-8.0 ppm (ArH); ¹⁹F NMR (564 MHz, [D₆]DMSO, 298 K): δ =-139.2, -150.0, -161.5 ppm; UV/Vis (THF, 0.02 mg mL⁻¹): λ_{max} =461 nm.

Preparation of HP3

Chromophore **M2** (84.6 mg, 0.10 mmol), **C1** (74.5 mg, 0.12 mmol). After the reaction had been stirred for 24 h, the end-capped chromophore **C1** was added for the next 24 h reaction. Red powder (86.4 mg, 58.9%); $M_w = 10.64 \times 10^4$, $M_w/M_n = 1.48$ (GPC, polystyrene calibration); IR (thin film): $\tilde{\nu} = 2127$ ($-N_3$), 1735 (C=O), 1518, 1340 cm⁻¹ ($-NO_2$); ¹H NMR (300 MHz, [D₆]DMSO, 298 K): $\delta = 1.8-2.4$ ($-CH_2-$), 2.8–3.0 ($-CH_2-$), 3.6–4.0 ($-N-CH_2-$), 4.0–4.6 ($-O-CH_2-$), 6.6–7.1 (ArH), 7.1–8.1 (ArH), 8.2–8.4 ppm (ArH); ¹⁹F NMR (564 MHz, [D₆]DMSO, 298 K): $\delta = -138.5$, -140.3, -142.1, -146.7, -151.8 ppm; UV/Vis (THF, 0.02 mgmL⁻¹): $\lambda_{max} = 463$ nm.

Preparation of HP4

Chromophore **M2** (84.6 mg, 0.10 mmol), **C2** (96.1 mg, 0.12 mmol). After the reaction had been stirred for 24 h, the end-capped chromophore **C1** was added for the next 24 h reaction. Red powder (99.1 mg, 60.2%); M_w =17.30×10⁴, M_w/M_n =2.15 (GPC, polystyrene calibration); IR (thin film): $\tilde{\nu}$ =2128 (-N₃), 1738 (C=O), 1520, 1340 cm⁻¹ (-NO₂); ¹H NMR (300 MHz, [D₆]DMSO, 298 K): δ =1.8–2.0 (-CH₂–), 2.0–2.4 (-CH₂–), 2.8–3.2 (-CH₂–), 3.8–4.1 (-*N*-CH₂–), 4.2–4.8 (-O-CH₂–), 6.9–7.2 (ArH), 7.2–8.1 (ArH), 8.4–8.6 ppm (ArH); ¹⁹F NMR (564 MHz, [D₆]DMSO, 298 K): δ =-138.6, -139.3, -140.3, -145.8, -146.8, -149.0, -151.9, -161.5 ppm; UV/Vis (THF, 0.02 mg mL⁻¹): λ_{max} =466 nm.

Preparation of Polymer Thin Films

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

NLO Measurements of Poled Films

The second-order optical nonlinearity of the polymers was determined by an in situ second harmonic generation (SHG) experiment by 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 (Table 1); voltage, 7.7 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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