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The self-assembly effect in NLO polymers containing isolation chromophores: enhanced NLO coefficient and stability†

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In this paper, a facile route was designed to prepare four new NLO polyaryleneethynylenes, which were constructed by two different chromophore moieties with the regular AB structure, to achieve a high NLO coefficient according to our recent work on ''isolation chromophores''. Meanwhile, normal aromatic rings or perfluoroaromatic rings were also introduced as isolation groups to investigate the aromatic/perfluoroaromatic (Ar–Ar^F) self-assembly effect in these NLO polymers. Thanks to the helpful self-assembly effect, the NLO effect and stability of **P2**, with perfluorophenyl groups as isolation groups, were improved to a large degree, in comparison with its analog **P1** containing normal phenyl groups as isolation groups.

Introduction

Organic second-order nonlinear optical (NLO) materials are actively pursued due to their increasing potential for applications in photonic devices, such as high-speed electro-optic modulators, optical switches and frequency converters.[1] For device applications, NLO polymers should possess large NLO activity, low optical loss, good temporal stability and processibility.[2] Among them, how to efficiently translate the large β values of the organic chromophores into high macroscopic NLO activities of polymers, are the major problems encountered in optimizing organic NLO materials.[3] On the basis of the site isolation principle proposed by Dalton and Jen *et al.*, since 2006, with an attempt to partially solve this challenge in NLO materials, we prepared different kinds of NLO polymers, in which the size of the isolation groups in the NLO chromophore moieties was changed from small to large. Based on the obtained experimental results, we proposed the concept of a "suitable isolation group", for the enhancement of the macroscopic NLO effect of polymers.[4] Based on the "site isolation principle" and the concept of a "suitable isolation group", many new concepts of NLO materials, such as "H-type" chromophores,[4a,5] "six branched" chromophores[6] and "star-type" chromphores,[7] *etc.*, have been proposed to enhance the NLO coefficient in recent years.

However, nearly all the isolation groups before 2012 were designed to only adjust the shape of the chromophore and decrease the strong interactions between the chromophore moieties, according to the "site isolation principle" and the concept of a "suitable isolation group". In fact, the interactions between two chromophores or two isolation groups should also be considered in the design of NLO materials. In 2012, for the first time, our group developed a new method by using the interactions between two chromophores: isolation chromophores.[8] The results showed that if the NLO polymer consists of two types of chromophore moieties with regular structures, its NLO coefficient could be improved by a large degree, in comparison with its analog just containing one type of chromophore (Chart S1, ESI†). On the other hand, different from normal aromatic rings, perfluoroaromatic rings were electropositive, and this activity could lead to the reversible self-assembly between these two types of aromatic rings. In 2007, this Ar–Ar^F self-assembly effect was first used in NLO materials by Jen and co-workers.[9] By utilizing aromatic/perfluoroaromatic dendron-substituted NLO chromophores in the presence of complementary Ar–Ar^F interactions, they developed a new class of molecular glasses (Chart S2, ESI†), which exhibited an improved poling efficiency and much enhanced macroscopic NLO effect. Very recently, these interactions between two types of isolation groups were also used in NLO polymers (Chart S3, ESI†), and a very large NLO coefficient has been achieved.[10]

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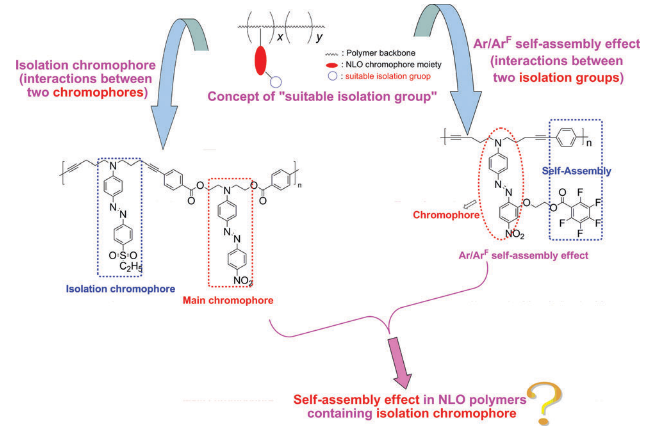


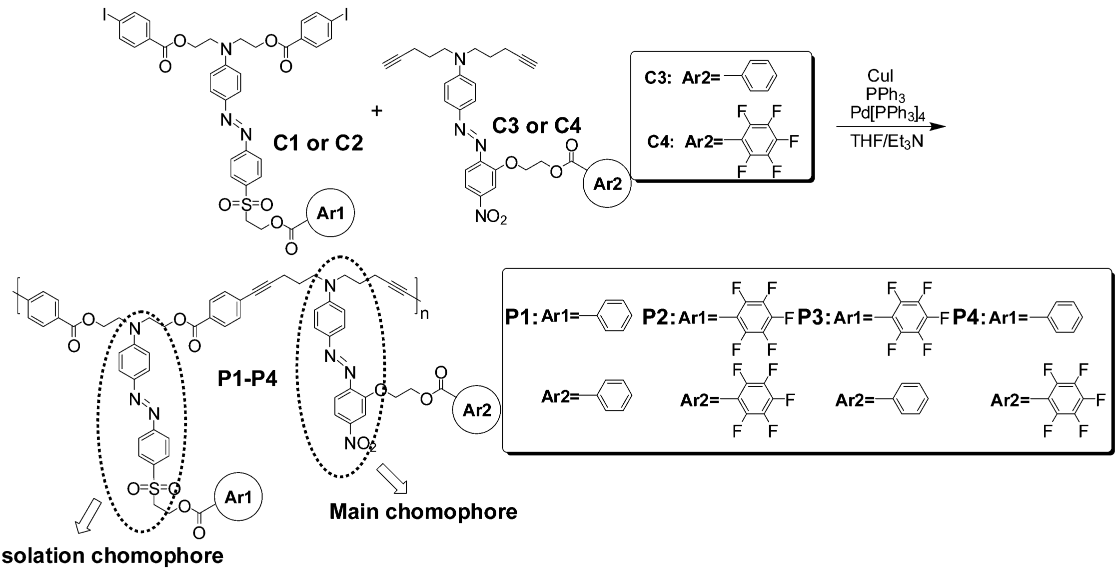
Chart 1 The original idea of this work.

How about the combination of these two new methods? Would the self-assembly effect work in the NLO polymers containing isolation chromophores? (Chart 1) However, so far, there was little work concerning it. Therefore, in this paper, we attempted to design a new series of NLO polymers (Scheme 1), in which two different types of NLO chromophores (sulfonyl- and nitro-based chromophores) were arranged. Meanwhile, the isolation groups in them were changed between aromatic and perfluoroaromatic to investigate the Ar–Ar^F self-assembly effect in these NLO polymers containing isolation chromophores. Excitingly, as the concentration of the pentafluorophenyl groups increased, the self-assembly effect became stronger, and the NLO effect and stability became better and better. In particular, the NLO coefficient of **P2**, with pentafluorophenyl as the isolation groups, was more than three times higher than that of **P1** which just contained normal phenyl groups, and its onset temperature for the decay in the d_{33} value was more than 40 °C higher than those of the other polymers, demonstrating the much better NLO stability, thanks to the Ar–Ar^F self-assembly effect. Herein, we would like to present the synthesis, characterization and properties of these NLO polymers in detail.

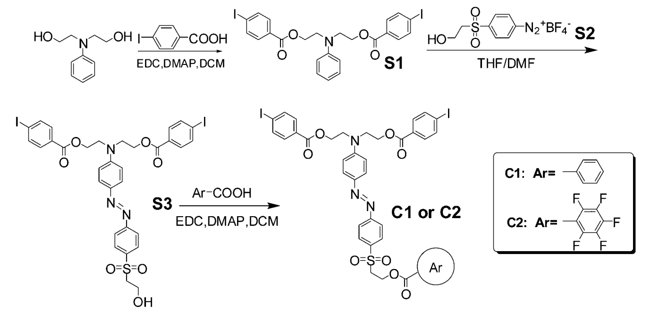
Result and discussion

Synthesis

The nitro chromophore-based monomers, **C3** and **C4**, have already been synthesized in our previous work,[10a,d] while the synthetic route to the sulfonyl chromophore-based monomer is presented in Scheme 2. The donor compound **S1** was prepared by esterification of *N*-phenyldiethanol and 4-iodobenzoic acid. The esterification is a simple reaction, and there are many reports in the literature concerned with the reaction using different catalysts, giving high yields. However, this reaction was not satisfied because of the poor solubility of the product **S1**. We tried to synthesize it according to our previous work, using dicyclohexylcarbodiimide (DCC) as the dehydrating agent, DMAP as the catalyst, CH_2Cl_2–THF as the solvent. However, because of the poor solubility of the product and DCC, 7 days later, the amount of product was only a little, as determined by thin layer chromatography (TLC). Thus, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC), with better solubility and much easier separation than DCC, was used as the dehydrating agent instead of DCC. Even so, the reaction still lasted 3 days with the providing the satisfactory yield at last. Under normal azo coupling reaction conditions, by using the diazonium fluoroborate as the azo-reagent, chromophore **S3** with the sulfonyl group as an acceptor was conveniently prepared. Finally, the monomers (chromophores **C1** and **C2**), containing different isolation groups, were yielded by the esterification of chromophore **S3** with benzoic acid or pentafluorobenzoic acid under mild conditions. It is worth pointing out that the solubility of the chromophores containing the donor **S1** units became



Scheme 1 Synthesis of the NLO polymers **P1–P4**.



Scheme 2 Synthesis of the monomers **C1** and **C2**.

improved after the introduction of the branched structure, and chromophores **C1** and **C2** could be dissolved in common polar solvents such as $CHCl_3$, CH_2Cl_2 and THF, *etc.*, making the polymerization convenient. At last, the target NLO polymer **P1–P4** could be prepared successfully *via* a typical Sonogashira cross-coupling reaction between the two corresponding chromophores, catalyzed by $Pd(PPh_3)_4$, PPh_3, and CuI, as shown in Scheme 1, which is similar to our previous work. Thus, the total route to the target polyaryleneethynylenes **P1–P4** was simple, making it convenient to compare their NLO properties.

Characterizations

The prepared chromophores and polymers were characterized by spectroscopic methods, and all gave satisfactory spectral data (see experimental section for detailed analysis data). NMR spectroscopy was an especially useful tool for illustrating the successful synthesis of the products in organic chemistry. Fig. 1 shows the ^{1}H NMR spectra of **C1**, **C3** and **P1**, as well as their chemical structures, as an example to illustrate the successful synthesis. In the ^{1}H NMR spectra of monomers **C1** and **C3**, no unexpected resonance peaks were observed, and the chemical shifts were consistent with the proposed structure (the corresponding peaks were marked in Fig. 1, 1–13 for **C1** while a–o for **C3**). After polymerization, all the peaks of **P1** showed an apparent inclination of signal broadening, and the disappearance of the single peaks associated with the protons of $C{\equiv}C\underline{H}$ (marked b in **C3**) at 2.06 ppm, again confirming the successful polymerization. The structures of the other polymers could be also confirmed in a similar way.

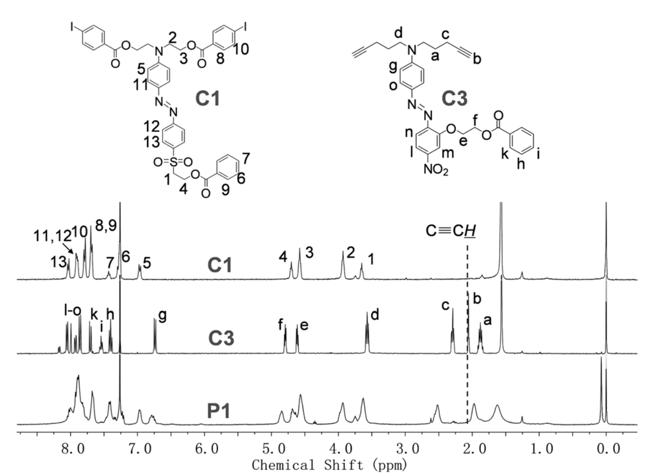


Fig. 1 ^{1}H NMR spectra of polymer **P1** and its corresponding monomers.

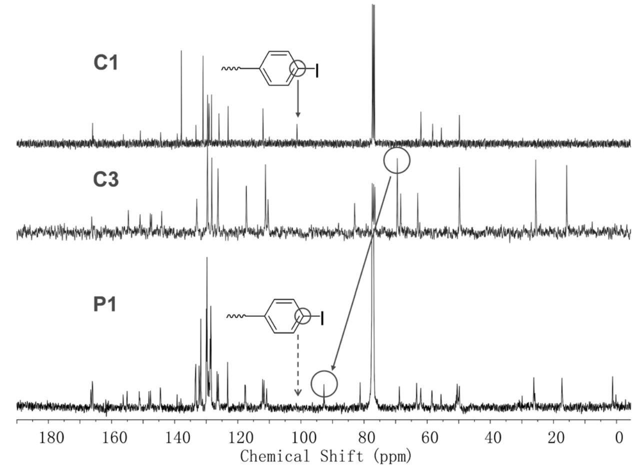


Fig. 2 ^{13}C NMR spectra of polymer **P1** and its corresponding monomers.

Here, the successful polymerization could be confirmed more obviously from their ^{13}C NMR spectra. Still using **P1** as a typical example, as shown in Fig. 2, in comparison with its monomers **C1** and **C3**, nearly all the peaks were still present in **P1**, except the characteristic peaks assigned to the functional groups of the monomers. For example: after polymerization the peak at 65.9 ppm (the typical signal of the $-C{\equiv}\underline{C}H$ group) moved to 92.7 ppm, indicating that the terminal alkynes in **C2** have been substituted by aromatic rings. In addition, the peak at 101.3 ppm, which was associated with iodobenzene, disappeared in the ^{13}C NMR spectra of **P1**, again confirming the successful polymerization.

This standpoint could be also confirmed by the FT-IR spectra. As shown in Fig. 3, after polymerization, the absorption band derived from the $C{\equiv}C{-}H$ stretching vibrations at about 3277 cm^{-1} in the FT-IR spectrum of chromophores **C3** disappeared in the spectrum of its corresponding polymer **P1**, while the peak at about 2150 cm^{-1} ($-C{\equiv}C-$) appeared, indicating the successful polymerization.

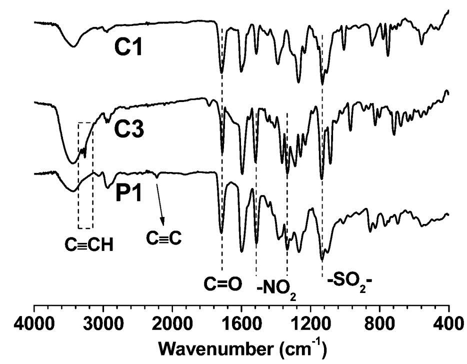


Fig. 3 FT-TR spectra of polymer **P1** and its corresponding monomers.

The ^{19}F NMR spectra were also used to investigate the Ar–Ar^F self-assembly effect in these NLO polymers. However, it was a pity that besides the three original peaks from the pentafluorophenyl group, no other signals appeared in their ^{19}F NMR spectra (Fig. S1, ESI†). On the other hand, it was evidence to confirm the chemical structure of these polymers.

The molecular weights of **P1–P4** were determined by gel-permeation chromatography (GPC) with THF as the eluent and polystyrene standards as the calibration standards. As shown in Table 1 and the experimental section, the weight-average molecular weights (M_w) of these polymers were nearly the same (around 12 000), with polydispersity indexes lying in the range of 1.54–1.62. These similar molecular weights could perhaps facilitate the comparison of their properties on the same level.

Their TGA thermograms are shown in Fig. S2 (ESI†), and the 5% weight loss temperature (T_d) of the polymers are listed in Table 1. All the polymers were thermally stable, with T_d values higher than 225 °C. Similar to our previous work on the Ar–Ar^F self-assembly effect,[10] **P2–P4**, bearing pentafluorophenyl groups as the isolation groups, exhibited a slightly worse thermal stability than **P1**, since the thermal stability of the pentafluorophenyl group was slightly worse than the normal phenyl one. However, this temperature (higher than 225 °C) was good enough for NLO materials, because the temperature for the real applications was generally lower than 200 °C. 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. As expected, as the concentration of pentafluorophenyl groups increased, the Ar–Ar^F self-assembly effect became stronger, and this interaction could result in a higher T_g value. For **P2**, its glass transition temperature was up to 158 °C, which is 37 °C higher than that of **P1**, which just contained normal phenyls as isolation groups. Furthermore, this higher T_g value could lead to the better stability of the NLO activity, which could contribute to the practical applications in photonics fields.

All the polymers were soluble in common polar organic solvents such as $CHCl_3$, CH_2Cl_2, THF, DMF, and DMSO. The UV-vis absorption spectra of these polymers in different solvents are demonstrated in Fig. 4 and S3–S6 (ESI†), and the maximum absorption wavelengths (λ_{max}) for the π–π* transition of the azo moieties are listed in Table S1 (ESI†). It was easily seen that the λ_{max} of the chromophore moieties in these polymers were nearly the same, since these four polymers consisted of the same chromophores. This phenomenon also indicated that the self-assembly effect did not occur between the perfluoroaromatic rings and chromophore moieties, or the λ_{max} for **P2–P4**, with the self-assembly effect in them, should be different from those of **P1** more or less. Thus, the self-assembly effect should only be present between the isolation groups and the benzene rings in the main polymer chains, similar to our previous work.[10a]

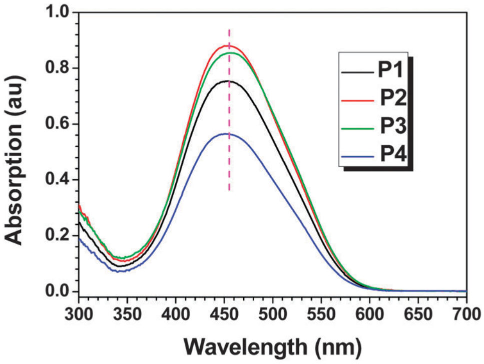


Fig. 4 UV-vis spectra of polymers **P1–P4** in THF solution (0.02 mg mL^{-1}).

Table 1 Characterization data of polymers **P1–P4**

No.	Yield (%)	M_w [a]	M_w/M_n [a]	T_g [b] (°C)	T_d [c] (°C)
P1	92.8	11 900	1.54	121	256
P2	70.0	12 800	1.56	158	225
P3	69.9	13 700	1.62	144	246
P4	87.6	10 400	1.56	142	231

[a] Determined by GPC in THF on the basis of a polystyrene calibration. [b] Glass transition temperature (T_g) of polymers detected by the DSC analyses under argon at a heating rate of 10 °C min^{-1}. [c] The 5% weight loss temperature of polymers detected by the TGA analyses under nitrogen at a heating rate of 10 °C min^{-1}.

NLO properties

The NLO coefficient is the most important parameter for NLO materials. In the excellent work of Jen's group,[9] as well as our recent work,[10] the complementary Ar–Ar^F interactions could improve the poling efficiency, leading to enhanced NLO activities. Thus, it was very important to check if this useful interaction could still work in NLO polymers containing isolation chromophore moieties. To evaluate the NLO activity of the polymers, their poled thin films were prepared. The most convenient technique to study the second-order NLO activity was to investigate the second harmonic generation (SHG) processes characterized by d_{33}, a SHG coefficient. The test procedure was similar to that reported previously,[11] and 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:[12]

$$\frac{d_{33,\mathrm{s}}}{d_{11,\mathrm{q}}} = \frac{\chi_\mathrm{s}^{(2)}}{\chi_\mathrm{q}^{(2)}} = \sqrt{\frac{I_\mathrm{s}}{I_\mathrm{q}}\frac{I_\mathrm{c,q}}{I_\mathrm{s}}}F$$

where $d_{11,q}$ is d_{11} of the quartz crystals, which is equal to 0.45 pm V^{-1}. 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 **P1–P4** were calculated at a fundamental wavelength of 1064 nm (Table 2). Generally, the d_{33} value of the same NLO polymer can be different when measured by different methods or different testing systems at different times. To avoid the above-mentioned possible deviations, the NLO properties of all the polymers were tested at the same time.

Table 2 NLO activities of polymers **P1–P4**

No.	T_e[a] (°C)	l_s[b] (μm)	d_{33}[c] (pm V^{-1})	$d_{33(\infty)}$[d] (pm V^{-1})	Φ[e]	N[f]
P1	125	0.26	27.9	4.9	0.08	0.519
P2	160	0.23	93.6	17.1	0.18	0.453
P3	130	0.26	45.3	8.1	0.11	0.484
P4	135	0.25	53.2	9.5	0.13	0.484

[a] The best poling temperature. [b] Film thickness. [c] Second harmonic generation (SHG) coefficient. [d] The nonresonant d_{33} values calculated using the approximate two-level model. [e] Order 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. [f] The loading density of the effective chromophore moieties.

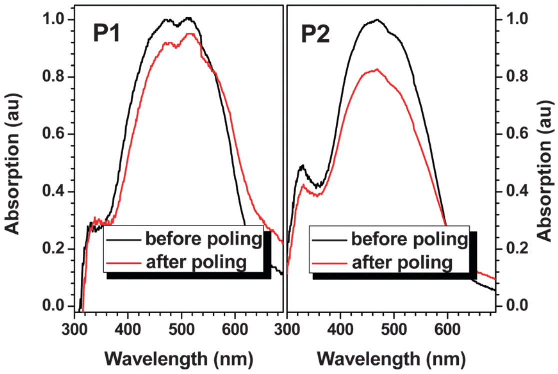


Fig. 5 Absorption spectra of the film of **P1** (left) and **P2** (right) before and after poling.

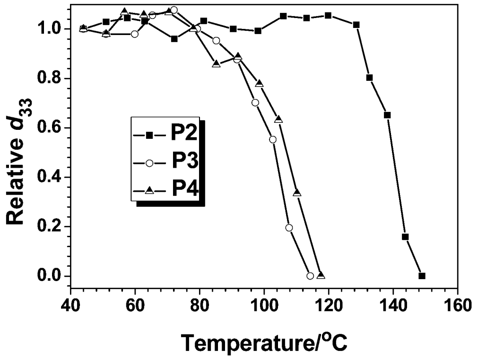


Fig. 6 Decay curves of the SHG coefficients of **P2–P4** as a function of the temperature.

The results were encouraging. As shown in Table 2, the d_{33} value of **P1**, with normal benzene rings as the isolation groups, was only 27.9 pm V^{-1}, and the d_{33} values increased to 45.3 and 53.2 pm V^{-1} in **P3** and **P4**, in which half of the isolation groups were changed to pentafluorophenyl groups. More excitingly, when the concentration of the pentafluorophenyl groups was further increased, the self-assembly effect became stronger, and the d_{33} value was further increased to 93.6 pm V^{-1} in **P2**, which is more than three times that of **P1**. The results showed that this powerful Ar–Ar^F self-assembly effect should also work in the NLO system containing isolation chromophores. Similar to our previous case,[10a] the enhanced NLO coefficient should be ascribed to the slightly different poling procedure with the Ar–Ar^F self-assembly effect (Fig. S7, ESI†): before poling, the chromophores were randomly arranged; when the temperature increased, the self-assembly effect from the Ar–Ar^F interactions was broken, if an electric field was added at that time, the chromophores could be induced into noncentrosymmetric alignment; after cooling, the self-assembly effect could be resumed, which could improve the stability of the NLO effect. This was consistent with the work of Jen *et al.* (Fig. S8, ESI†). Meanwhile, in comparison with our previous work on the NLO polymers, also using nitro-based azobenzene as the chromophore, containing normal suitable isolation groups (some examples are shown in Chart S4, ESI†), 93.6 pm V^{-1} was still a high value, confirming the advantages of the self-assembly effect and isolation chromophore once again.

Since the films of the polymers still had some absorptions at the wavelength of 532 nm (double the frequency of the 1064 nm fundamental wavelength), the NLO properties of **P1–P4** should be much smaller, as shown in Table 2 ($d_{33(\infty)}$ values), which were calculated using the approximate two-level model.[13] Since all the polymers exhibited almost the same UV-vis spectra, their $d_{33(\infty)}$ values demonstrated the same phenomena as their d_{33} values.

To further study the alignment behaviour of the chromophore moieties in the polymers, the order parameter (Φ) of the polymers (Table 2) was measured and calculated from the change of the UV-vis spectra of their films before and after poling under an electric field (Fig. 5 and Fig. S6 and S7, ESI†), according to the equation described in Table 2 (footnote e). The tested Φ value of **P2** (0.18) was still much higher than that of **P1** (0.08), indicating the better alignment of the chromophore moieties in the poled thin film of **P2**, further confirming the advantages of the self-assembly effect in NLO polymers. As expected, the Φ values of **P3** and **P4** were tested to be 0.11 and 0.13, respectively, which are between the values of **P1** and **P2**.

The dynamic thermal stabilities of the NLO activities of the polymers were investigated by depoling experiments,[14] in which the real-time decays of their SHG signals were monitored as the poled films were heated from 40 to 160 °C in air at a rate of 4 °C min^{-1}. Fig. 6 shows the decay of the SHG coefficient of **P2–P4** as a function of temperature. Since the SHG signal of **P1** was low, its depoling experiment was not successful. Even so, it was very easy to see that the onset temperatures for the decay in the d_{33} value of **P2** was much higher than that of **P3** and **P4**. This was understandable: due to the strong Ar–Ar^F self-assembly effect, which destroys the alignment of the chromophore moieties in **P2**, much more energy should be needed. This should be treated as important evidence that confirms the existence of the Ar–Ar^F self-assembly effect in this series of polymers containing isolation chromophores. Furthermore, the high T_{onset} value of **P2** (up to 132 °C) indicated that the long-term temporal stability was relatively good,[13] which was beneficial to its practical NLO applications.

Conclusions

In summary, a facile route was designed to prepare four new NLO polyaryleneethynylenes containing isolation chromophores *via* the simple Sonogashira coupling reaction. Meanwhile, different types of isolation chromophores (normal aromatic and perfluoroaromatic rings) were also introduced to investigate the Ar–Ar^F self-assembly effect in these NLO polymers. Thanks to the powerful self-assembly effect, the NLO coefficient of **P2** was more than three times that of its analog **P1** with normal phenyl groups as the isolation groups. The onset temperatures for the decay in the d_{33} value of **P2** was up to 132 °C, demonstrating the much better stability of the NLO activity than that of **P1**. These results showed that the powerful Ar–Ar^F self-assembly effect could also work in the NLO systems containing isolation chromophores. Further research on the applications of this conclusion to dendritic macromolecules are in progress in our laboratory.

Experiment

Materials

Tetrahydrofuran (THF) was dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen. Triethylamine (Et_3N) was distilled under normal pressure and kept over potassium hydroxide. Dichloromethane (CH_2Cl_2, DCM) was dried over CaH_2 and distilled under normal pressure before use. Nitro chromophore based monomers **C3** and **C4** have been prepared in our previous work.[10a,d] All the other reagents were used as received.

Instrumentation

NMR spectra were measured on a Varian Mercury300 or Bruker ARX 400 spectrometer using tetramethylsilane (TMS; δ = 0 ppm) as the internal standard. ^{19}F NMR spectra were measured on a Varian Mercury600 spectrometer. The Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000–400 cm^{-1}. UV-vis spectra were obtained using a Shimadzu UV-2550 spectrometer. Elemental analyses (EA) were performed by a CARLOERBA-1106 microelemental analyzer. Gel permeation chromatography (GPC) was used to determine the molecular weights of the polymers. GPC analysis was performed on a Waters HPLC system equipped with a 2690D separation module and a 2410 refractive index detector. Polystyrene standards were used as calibration standards for GPC. THF was used as an eluent, and the flow rate was 1.0 mL min^{-1}. Thermal analysis was performed on a NETZSCH STA449C thermal analyzer at a heating rate of 10 °C min^{-1} in nitrogen at a flow rate of 50 cm^3 min^{-1} for thermogravimetric analysis (TGA) and the thermal transitions of the polymers. The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

Syntheses

Compound S1. *N*-Phenyldiethanolamin (1.08 g, 6.0 mmol), 4-iodobenzoic acid (4.46 g, 18.0 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (4.60 g, 24.0 mmol), and 4-(*N*,*N*-dimethyl)aminopyridine (DMAP) (288 mg, 2.40 mmol) were dissolved in dry CH_2Cl_2 (120 mL) and stirred at room temperature for 3 days, and then treated with a saturated solution of citric acid and extracted with CH_2Cl_2, washed with brine and a saturated solution of citric acid. After the removal of all the solvent, the crude product was recrystallized from a lot of acetone to afford a white solid (3.80 g, 98.8%). ^{1}H NMR (300 MHz, DMSO-d_6, 298 K), δ (TMS, ppm): 3.79 (t, J = 5.1 Hz, 4H, -NCH_2-), 4.41 (t, J = 5.1 Hz, 4H, -OCH_2-), 6.63 (t, J = 7.2 Hz, 1H, ArH), 6.88 (d, J = 8.4 Hz, 2H, ArH), 7.17 (t, J = 7.8 Hz, 2H, ArH), 7.63 (d, J = 8.1 Hz, 4H, ArH), 7.87 (d, J = 8.1 Hz, 4H, ArH). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K), δ (ppm): 50.4, 64.1, 103.6, 113.7, 117.9, 130.6, 130.8, 132.5, 139.3, 149.0, 167.1.

Compound S3

Compound **S1** (897 mg, 1.40 mmol) and diazonium salt **S2** (420 mg, 1.40 mmol) were dissolved in DMF/THF (15 mL/15 mL) at 0 °C. The reaction mixture was stirred for 36 h at 0 °C, and then treated with H_2O and extracted with a lot of $CHCl_3$, washed with brine. The organic layer was dried over anhydrous sodium sulfate. After the removal of all the organic solvent, the crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (60–90 °C) (2/3, v/v) as eluent and then recrystallized from ethyl acetate to afford an orange solid (980 mg, 82.2%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 2.76 (s, br, 1H, –OH), 3.40 (s, br, –SCH_2–, 2H), 3.92 (s, br, –NCH_2–, 4H), 4.04 (s, br, –OCH_2–, 2H), 4.57 (s, br, –$COOCH_2$–, 4H), 6.96 (d, J = 8.4 Hz, 2H, ArH), 7.68 (d, J = 7.5 Hz, 4H, ArH), 7.79 (d, J = 7.5 Hz, 4H, ArH), 7.92 (d, J = 8.1 Hz, 2H, ArH), 8.02 (m, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K), δ (ppm): 49.47, 56.09, 58.21, 61.83, 101.13, 111.80, 122.81, 125.87, 128.84, 130.79, 137.63, 138.41, 144.07, 150.76, 156.00, 165.78.

Chromophore C1. Compound **S3** (213 mg, 0.25 mmol), benzoic acid (45.8 mg, 0.375 mmol). 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (95.9 mg, 0.50 mmol), and 4-(*N*,*N*-dimethyl)aminopyridine (DMAP) (6.1 mg, 0.050 mmol) were dissolved in 10 mL dry CH_2Cl_2 and stirred at room temperature for 3 h, and then treated with saturated solution of citric acid and extracted with CH_2Cl_2, washed with brine and a saturated solution of citric acid. After the removal of all the solvent, the crude product was purified by column chromatography on silica gel using ethyl acetate–chloroform (1/15, v/v) as eluent to afford an orange solid (213.6 mg, 89.2%). IR (KBr), ν (cm^{-1}): 1716 (C═O), 1132 (–SO_2). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 3.65 (s, br, 2H, –SCH_2–), 3.93 (t, J = 8.0 Hz, 4H, –NCH_2–), 4.58 (t, J = 8.0 Hz, 4H, –$COOCH_2$–), 4.70 (t, J = 8.0 Hz, 2H, –$COOCH_2$–), 6.95 (d, J = 8.0 Hz, 2H, ArH), 7.26 (m, 2H, ArH), 7.43 (s, br, 1H, ArH), 7.69 (d, J = 8.0 Hz, 4H, ArH), 7.79 (d, J = 8.0 Hz, 4H, ArH), 7.91(m, 4H, ArH), 8.02 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ (ppm): 49.78, 55.51, 58.29, 61.98, 101.25, 112.3, 123.07, 125.97, 128.93, 131.01, 137.89, 139.17, 144.44, 150.86, 156.23, 166.00. $C_{39}H_{33}N_3O_8SI_2$ (EA) (%, found/calcd): C, 49.02/48.92; H, 3.63/3.47; N, 4.22/4.39.

Chromophore C2. The procedure was similar to the synthesis of chromophore **C1**. Compound **S3** (213 mg, 0.25 mmol), pentafluorobenzoic acid (79.5 mg, 0.375 mmol). The crude product was purified by column chromatography on silica gel using ethyl acetate/chloroform (1/20, v/v) as eluent to afford a red solid (233.2 mg, 89.0%). IR (KBr), ν (cm^{-1}): 1736 (C═O), 1130 (–SO_2). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (TMS, ppm): 3.55 (s, br, 2H, –SCH_2–), 3.86 (t, J = 8.0 Hz, 4H, –NCH_2–), 4.51

(t, J = 8.0 Hz, 4H, –COOCH$_2$–), 4.66 (t, J = 8.0 Hz, 2H, –COOCH$_2$–), 6.90 (d, J = 8.0 Hz, 2H, ArH), 7.69 (d, J = 8.0 Hz, 4H, ArH), 7.79 (d, J = 8.0 Hz, 4H, ArH), 7.91 (m, 4H, ArH), 8.02 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR (100 MHz, CDCl$_3$, 298 K), δ (ppm): 48.71, 53.93, 58.72, 60.98, 100.2, 110.99, 121.68, 125.04, 128.01, 128.15, 129.98, 136.86, 137.92, 143.39, 150.05, 155.25, 164.96. ^{19}F NMR (376 MHz, CDCl$_3$, 298 K), δ (ppm): −137.27, −146.74, −159.84. $C_{39}H_{28}F_5N_3O_8SI_2$ (EA) (%, found/calcd): C, 44.54/44.72; H, 2.87/2.69; N, 4.13/4.01.

General procedure for P1–P4. A mixture of chromophore **C1** or **C2** (1.00 equiv.), chromophore **C3** or **C4** (1.00 equiv.), copper iodide (CuI) (5 mol%), tetrakis(triphenylphosphine)palladium (Pd(PPh$_3$)$_4$) (3 mol%) and triphenylphosphine (PPh$_3$) (5 mol%) was carefully degassed and charged with argon. THF/Et$_3$N (9/1, v/v, concentration: 0.02 mmol mL^{-1} **C1** or **C2** in THF) was then added. The reaction was stirred for 4 days at room temperature. The mixture was passed through a cotton filter and dropped into a lot of methanol. The precipitate was collected, further purified by several precipitations of its THF solution into acetone, and dried in a vacuum at 40 °C to a constant weight.

P1. Chromophore **C1** (95.7 mg, 0.10 mmol), chromophore **C3** (53.8 mg, 0.10 mmol), **P1** was obtained as a red powder (115.2 mg, 92.8%). M_w = 11 900, M_w/M_n = 1.54 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 1719 (C=O), 1517, 1338 (–NO$_2$), 1132 (–SO$_2$). ^{1}H NMR (400 MHz, CDCl$_3$ 298 K), δ (TMS, ppm): 1.8–2.1 (–CH$_2$–), 2.4–2.6 (–CH$_2$–), 3.5–3.7 (–SCH$_2$–), 3.8–4.0 (–NCH$_2$–), 4.4–4.7 (–OCH$_2$– and –COOCH$_2$–), 6.6–6.7 (ArH), 6.9–7.0 (ArH), 7.2–7.6 (ArH), 7.6–7.7 (ArH), 7.8–8.1 (ArH). ^{13}C NMR (75 MHz, CDCl$_3$, 298 K), δ (ppm): 17.30, 26.25, 49.82, 50.51, 55.62, 58.49, 62.03, 63.35, 68.82, 81.25, 92.71, 110.87, 111.72, 112.14, 117.61, 117.76, 123.24, 126.22, 126.61, 128.57, 128.78, 129.32, 129.77, 129.95, 131.76, 132.20, 132.27, 132.34, 133.50, 139.23, 144.57, 147.67, 148.17, 151.24, 155.07, 156.36, 166.1, 166.58.

P2. Chromophore **C2** (80.6 mg, 0.077 mmol), chromophore **C4** (48.4 mg, 0.077 mmol), **P2** was obtained as red powder (76.7 mg, 70.0%). M_w = 12 800, M_w/M_n = 1.56 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 1729 (C=O), 1518, 1337 (–NO$_2$), 1130 (–SO$_2$). ^{1}H NMR (400 MHz, CDCl$_3$ 298 K), δ (TMS, ppm): 1.8–2.1 (–CH$_2$–), 2.4–2.6 (–CH$_2$–), 3.5–3.7 (–SCH$_2$–), 3.8–4.0 (–NCH$_2$–), 4.4–4.6 (–OCH$_2$–), 4.7–4.8 (–COOCH$_2$–), 6.6–6.7 (ArH), 6.8–6.9 (ArH), 7.3–7.4 (ArH), 7.5–7.6 (ArH), 7.7–8.0 (ArH). ^{13}C NMR (75 MHz, CDCl$_3$, 298 K), δ (ppm): 16.00, 24.93, 48.59, 49.24, 60.80, 63.17, 66.95, 79.99, 91.43, 109.25, 110.32, 110.90, 116.54, 121.91, 124.94, 125.26, 126.85, 127.55, 127.91, 128.48, 130.45, 137.37, 138.07, 143.22, 146.40, 153.45, 164.81. ^{19}F NMR (564 MHz, CDCl$_3$, 298 K), δ (ppm): −137.81, −148.46, −160.70.

P3. Chromophore **C2** (94.2 mg, 0.090 mmol), chromophore **C3** (48.4 mg, 0.090 mmol), **P3** was obtained as red powder (83.3 mg, 69.9%). M_w = 13 700, M_w/M_n = 1.62 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 1726 (C=O), 1516, 1339 (-NO$_2$), 1131 (-SO$_2$). ^{1}H NMR (400MHz, CDCl$_3$ 298 K), δ (TMS, ppm): 1.7–2.0 (–CH$_2$–), 2.4–2.5 (–CH$_2$–), 3.4–3.6 (–SCH$_2$–), 3.7–4.0 (–NCH$_2$–), 4.3–4.5 (–OCH$_2$–), 4.6–4.7 (–COOCH$_2$–), 6.6–6.7 (ArH), 6.8–6.9 (ArH), 7.3–7.4 (ArH), 7.5–8.0 (ArH). ^{13}C NMR (75 MHz, CDCl$_3$, 298 K), δ (ppm): 16.12, 25.11, 45.83, 48.75, 49.32, 60.98, 62.16, 67.79, 80.09, 91.48, 100.18, 110.56, 110.99, 116.41, 116.62, 121.98, 124.99, 125.37, 127.39, 127.64, 128.04, 128.77, 130.00, 132.08, 130.57, 132.08, 136.87, 137.60, 138.29, 143.49, 146.59, 147.08, 150.04, 153.92, 155.13, 164.88, 165.37. ^{19}F NMR (564 MHz, CDCl$_3$, 298 K), δ (ppm): −137.81, −148.45, −160.70.

P4. Chromophore **C1** (86.2 mg, 0.090 mmol), chromophore **C4** (56.6 mg, 0.090 mmol), **P4** was obtained as red powder (104.8 mg, 87.6%). M_w = 10 400, M_w/M_n = 1.56 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 1726 (C=O), 1517, 1339 (–NO$_2$), 1132 (–SO$_2$). ^{1}H NMR (400 MHz, CDCl$_3$ 298 K), δ (TMS, ppm): 1.7–2.0 (–CH$_2$–), 2.3–2.5 (–CH$_2$–), 3.5–3.7 (–SCH$_2$–), 3.8–4.0 (–NCH$_2$–), 4.3–4.7 (–OCH$_2$–), 4.8–4.9 (–COOCH$_2$–), 6.7–6.8 (ArH), 6.9–7.0 (ArH), 7.2–7.4 (ArH), 7.6–7.7 (ArH), 7.8–8.1 (ArH). ^{13}C NMR (75 MHz, CDCl$_3$, 298 K), δ (ppm): 17.27, 26.17, 49.82, 50.48, 51.06, 55.65, 58.51, 62.08, 64.40, 68.14, 81.25, 92.71, 110.42, 111.55, 112.14, 112.71, 117.80, 123.24, 126.20, 126.54, 128.51, 128.71, 129.03, 129.33, 129.61, 129.77, 131.22, 131.58, 131.74, 132.27, 133.51, 138.06, 139.23, 144.46, 146.57, 147.66, 148.17, 151.04, 154.69, 156.37, 165.97. ^{19}F NMR (564 MHz, CDCl$_3$, 298 K), δ (ppm): −137.81, −148.45, −160.70.

Preparation of polymer thin films

The polymers **P1–P4** were dissolved in THF (concentration ~3 wt%), and the solutions were filtered through syringe filters. Polymer films were spin coated onto indium–tin–oxide (ITO)-coated glass substrates, which were cleaned by DMF, acetone, distilled water, and THF sequentially in an ultrasonic bath before use. Residual solvent was removed by heating the films in a vacuum oven at 40 °C.

NLO measurement of poled films

The second-order optical nonlinearity of the polymers was determined by an *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 (Table 2); voltage, 7.8 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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