

Improved Nonlinearity—Transparency— Thermal Stability Trade-Off with Spirobifluorene-Bridged Donor- π -Acceptor Chromophores

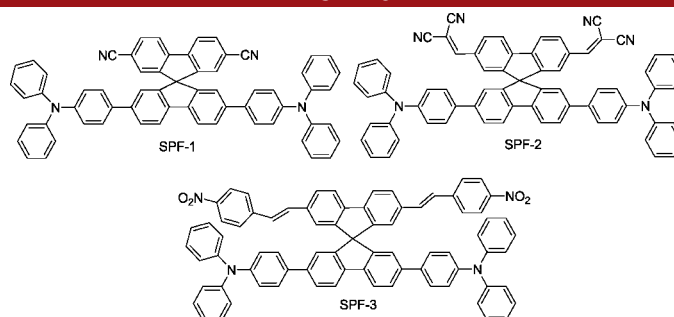
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ABSTRACT



A series of novel 9,9'-spirobifluorene-bridged donor- π -acceptor chromophores containing triarylamine moieties were easily synthesized starting from the readily available reagent 4,4'-dimethylbiphenyl. These chromophores were found to combine excellent transparency in the visible region, high thermal stabilities, and large optical nonlinearity.

In recent years the design and synthesis of organic compounds that exhibit nonlinear optical (NLO) properties (first and second hyperpolarizability β and γ , respectively) have received particular attention because of their possible applications in various fields, including telecommunications, optical data storage, optical power limiting, etc. This interest is motivated not only by the large NLO response but also by the versatility, ease of processing, and possibility of tailoring the physicochemical properties by the molecular engineering approach.¹ To date, the vast majority of performing NLO chromophores obey a few general structural requirements: they are planar conjugated structures end-capped with strong electron-donor (D) and electron-acceptor (A) residues leading to effective polarization along the π -conjugated axis.² Although, increasing π -conjugation generally translates into higher molecular hyperpolarizability, the increase in molecular hyperpolarizability of such

chromophores is usually accompanied by a decrease in the optical transparency and thermal stability, which limits their practical applications in photonics.^{3,4} As a consequence, a variety of dual (multiple) charge-transfer chromophores, such as octupolar, Λ -shaped, and X-shaped molecules have been designed and investigated in recent years.⁵ However, achieving the nonlinearity—transparency—thermal stability trade-off is still a major challenge.^{2,5}

Recently, three-dimensional materials based on spirobifluorene-bridged conjugated systems became of particular interest.⁶ Generally, spiro compounds are known as glass-forming materials with a high thermal stability.⁷ The introduction of electron donor and electron acceptor groups in

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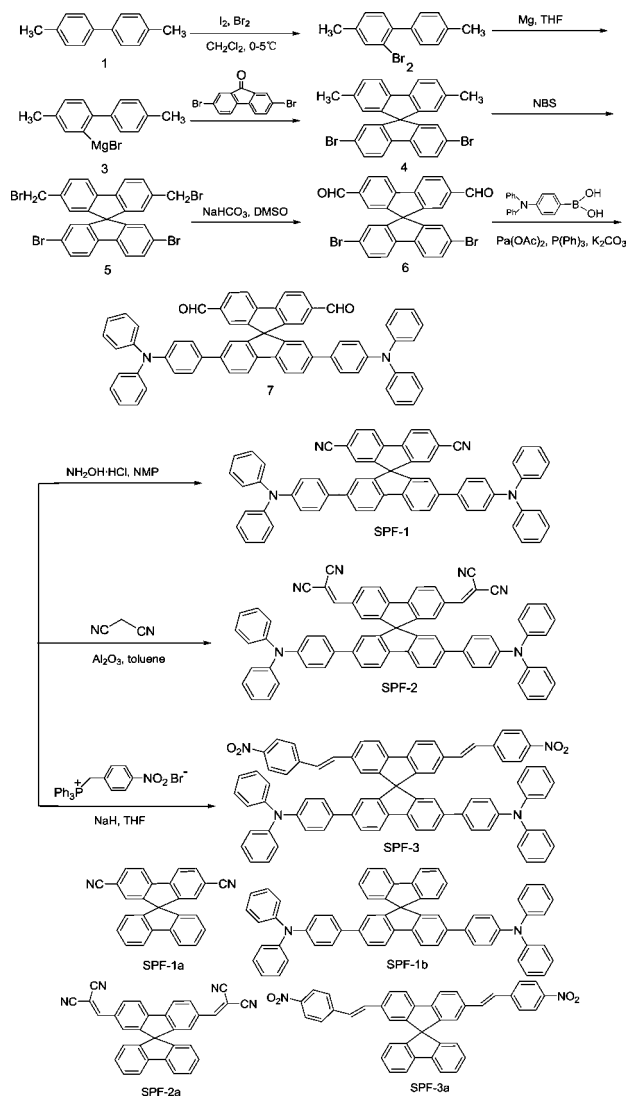
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two different biphenyl branches of the spirobifluorene core affords a class of spiro compounds with a “top-down” asymmetric 2, 7-A, 2', 7'-D substitution pattern,⁸ which may be good candidates for the construction of highly transparent NLO materials due to the spiroconjugation effects between the two fluorene units.^{9,10} Most spiro-linked compounds are synthesized from the central spirobifluorene with equal or different substituents in the 2,2' and 7,7' positions,^{8,11} but it is difficult to obtain “top-down” asymmetric compounds directly from the spirobifluorene core. Some groups reported the synthesis of “top-down” asymmetric spiro compounds by introducing halogeno groups in the precursor 9, 9'-fluorenone before spiro linkage.⁸

Scheme 1. Reagents and Conditions



In this communication, we synthesized three new “top-down” asymmetric spirobifluorene compounds, **SPF-1**, **SPF-2**, and **SPF-3** starting from 4,4'-dimethylbiphenyl.

The advantages of this synthetic method are that it avoids the use of expensive reagent 2-bromobiphenyl as the starting material and the methyl group is convenient for subsequent transformations to appropriate functional groups such as bromomethyl, aldehyde, carboxylic acid, etc. The synthetic pathways of 9,9'-spirobifluorene-bridged D- π -A chromophores **SPF-1**, **SPF-2**, and **SPF-3** are shown in Scheme 1. In these D- π -A chromophores, the cyano, dicyanomethylene, and nitrophenyl vinyl groups serve as the electron acceptor, respectively, while the triarylamine moiety acts as the donor counterpart. The role being played by spirobifluorene is as a π -conjugated bridge because of the presence of the spiroconjugation effect between the electron acceptor and the donor. For the purpose of comparison, four model compounds **SPF-1a**, **SPF-2a**, **SPF-3a**, and **SPF-1b** (Scheme 1) have been chosen as the reference compounds in this work. **SPF-1**, **SPF-2**, and **SPF-3** are distinguished by good transparency, high thermal stability, and large optical nonlinearity for nonlinear optical application. We emphasize that although a few “top-down” asymmetric spirobifluorene compounds have been synthesized by several groups^{6,12–14} and many asymmetric spirobifluorene compounds have been employed as NLO materials,¹⁵ the potentialities of “top-down” asymmetric spirobifluorene compounds for NLO have not been considered yet.¹⁵

The UV–vis absorption spectra of the chromophores **SPF-1**, **SPF-2**, and **SPF-3** and model compounds **SPF-1a**, **SPF-2a**, **SPF-3a**, and **SPF-1b** in toluene are shown in Figure 1. It can be seen that the maximum absorption wavelengths of **SPF-1**, **SPF-2**, and **SPF-3** are less than

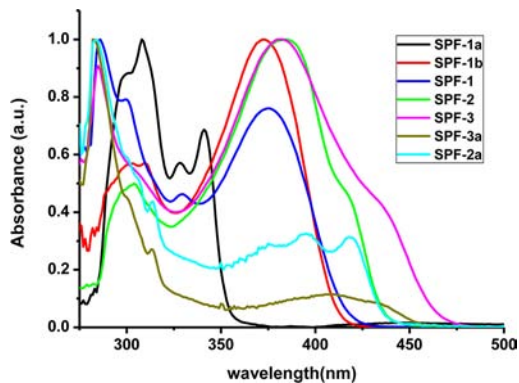


Figure 1. UV–vis spectra of chromophores in toluene.

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400 nm and the cutoff wavelengths were found to be as low as 460 nm. Accordingly, these molecules maintain almost full transparency in the visible region. We observed two distinct absorption bands in the absorption spectra of **SPF-1**, **SPF-2**, and **SPF-3**: one in the range 280–320 nm, corresponding to the π - π^* electronic transition of the spirobifluorene core, and the other in the range 350–460 nm, corresponding to the intramolecular charge transfer (ICT) band, as confirmed by the solvatochromism (Table 1, Supporting Information (SI)).^{15,16} The ICT bands red-shifted in the order **SPF-1** < **SPF-2** \approx **SPF-3**. The absorption maxima for the dicyanovinyl substituted **SPF-2** and that of the 4-nitrostyryl analog **SPF-3** appear at nearly similar λ_{\max} (around 384 nm), thereby suggesting their comparable electron-withdrawing properties.³ In general, the absorption spectra of the target compound exhibit a composite characteristic of the acceptor and donor spirobifluorene model compounds, with negligible interactions among the substituents in the ground state.^{6,17} In contrast, the absorption

Table 1. Linear and Nonlinear Properties of the Chromophores and Their Thermal Stabilities

comps	λ_{\max}^a (nm)	λ_{\max}^b (nm)	ΔV^c (cm ⁻¹)	$\beta_{CT} \mu_g \times 10^{-30}$ (esu D) ^d	σ^e (GM)	T_d^f (°C)
SPF-1a	338	341	243			
SPF-1b	370	372	275			
SPF-1	368	376	626	19138	62949	268
SPF-2	376	384	626	12429	2928	264
SPF-3	378	384	554	15134	3773	235
DR1	477 ^g	503 ^h	1083	4340		235 ⁱ

^aIn acetonitrile, the absorption data were taken from the first vibronic peak. ^bIn toluene, the absorption data were taken from the first vibronic peak. ^cSolvatochromic shift = $1/\lambda_{\max}(\text{acetonitrile}) - 1/\lambda_{\max}(\text{toluene})$. ^dThe values were measured by the solvatochromic method. ^eThe two-photon absorption cross sections. ^fDetermined by TGA. ^gMeasured in 1,4-dioxane; the λ_{\max} value of **DR1** is from ref 27. ^hMeasured in DMF; the λ_{\max} value of **DR1** is from ref 27. ⁱThe T_d value of **DR1** is from ref 24.

profiles of the **SPF** compounds (**SPF-1**, **SPF-2**, and **SPF-3**) are different from those of the model compounds (**SPF-1a**, **SPF-2a**, **SPF-3a**, and **SPF-1b**). Careful spectral analyses (from Figure 1 and Table 1) indicate that the lowest energy absorption of **SPF-1** displays a bathochromic shift and exhibits a more pronounced solvatochromism as compared to those of monochromophore model compounds **SPF-1a** and **SPF-1b**. From Figure 1, it can be seen that the lowest energy absorptions of **SPF-2** and **SPF-3** in toluene appear at shorter wavelengths than those of **SPF-2a** (at 418 nm) and **SPF-3a** (at \sim 410 nm), respectively. Such a hypsochromic shift of the lowest energy absorption can be observed in other spiro-bridged conjugated systems.^{18,19} These results can be

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noted as evidence for the interaction between the upper and lower parts of the molecule in the ground state.^{13,19–23}

The thermal stabilities of **SPF-1**, **SPF-2**, and **SPF-3** are investigated by thermal gravity analysis (TGA) and differential scanning calorimetry (DSC). The decomposition temperature (T_d , temperature at which 5% mass loss occurs during heating), as shown in Figure 2, is 268 °C for **SPF-1**, 264 °C for **SPF-2**, and 235 °C for **SPF-3**, respectively. Their T_d 's are very close to those of commercially available NLO dyes, such as **DR1** ($T_d = 254$ °C), **DO3** ($T_d = 235$ °C), and **DR19** ($T_d = 260$ °C),²⁴ and consistent with the appropriate temperature for materials working and processing.²⁵ The decomposition temperature of chromophore **SPF-3** was decreased due to its greater degree of π -electron conjugation. With extension of the π -conjugation system comes an increased thermal instability of the compounds.²⁶ No melting was noticed for chromophores **SPF-1**, **SPF-2**, and **SPF-3** in the DSC curves (see SI), and an obvious exothermic peak due to crystallization of **SPF-1** at 240 °C is observed.

The TPA cross sections of chromophores **SPF-1**, **SPF-2**, and **SPF-3** have been measured by open aperture Z-scan experiments performed with a femtosecond (fs) laser

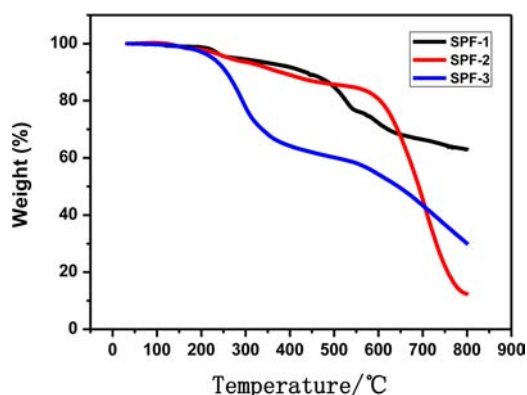


Figure 2. TGA curves of **SPF-1**, **SPF-2**, and **SPF-3**.

source. Figure 3 shows the Z-scan data of chromophores **SPF-1**, **SPF-2**, and **SPF-3** in THF at the nonoptimized 800 nm wavelength position. The σ -values of **SPF-1**, **SPF-2**, and **SPF-3** were 62949 GM, 2928 GM, and 3773 GM respectively. With respect to the π -attached acceptor

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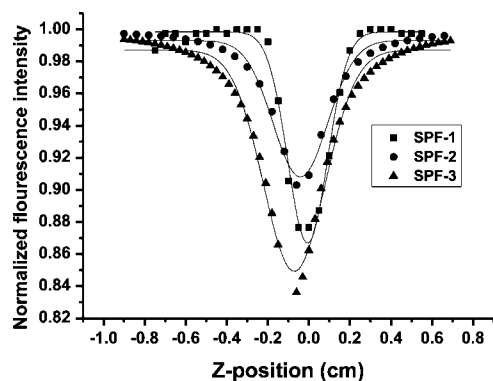


Figure 3. Z-scan experimental data of chromophores **SPF-1** (10^{-3} M), **SPF-2** (10^{-2} M), and **SPF-3** (10^{-2} M) in THF.

chromophores, the σ -values of **SPF-1**, **SPF-2**, and **SPF-3** followed the order dicyanovinyl < 4-nitrostyryl < -CN. A higher σ -value is recorded for the case of **SPF-1** although its ICT band is lower compared to those of **SPF-2** and **SPF-3** (Figure 1). This observation implies that factor(s) other than molecular polarizability contribute in part to the nonlinear optic effect.³

It is known that the second-order polarizabilities (β_{xxx}), the composite magnitude ($\beta_{CT}\mu_g$) of molecular hypersusceptibilities, and the second harmonic generation (SHG) values of microcrystals are usually used to characterize the second-order NLO performance of organic compounds. The most common method used to measure organic compounds is the EFISHG or HRS method, but this experimentation is not easy to set up in most laboratories.

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We report here the measurement and calculation of the values of $\beta_{CT}\mu_g$ using the solvatochromic method (see SI),^{27–29} although the values obtained are not as accurate as the values measured with the EFISHG or HRS method. The experimental values of **SPF-1**, **SPF-2**, **SPF-3**, and **DRI** are listed in Table 1, where **DRI** data have been enclosed as reference. It can be found that the values of **SPF-1**, **SPF-2**, and **SPF-3** were 19138 esu D, 12429 esu D, and 15134 esu D, respectively, larger than that of **DRI**. The evolution of the second-order NLO properties of **SPF-1**, **SPF-2**, and **SPF-3** with the changes in the acceptor follows a similar tendency to that of two-photon absorption properties.

In summary, we have easily synthesized a series of novel 9,9'-spirobifluorene-bridged D- π -A chromophores containing triarylamine moieties starting from the readily available reagent 4,4'-dimethylbiphenyl and demonstrated that the introduction of electron donor and acceptor groups in two different fluorene units of the spiro-bridged conjugated systems provides a promising and innovative route for the optimization of the nonlinearity–transparency–thermal stability trade-off.

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Supporting Information Available. Experimental procedures and characterization for **4–7**, **SPF-1**, **SPF-2**, and **SPF-3**. Copies of ^1H and ^{13}C NMR spectra. Determination of the second-order molecular nonlinearity and thermal stabilities. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.