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# A bistriphenylamine-substituted spirobifluorene derivative exhibiting excellent nonlinearity/transparency/thermal stability trade-off and strong two-photon induced blue fluorescence

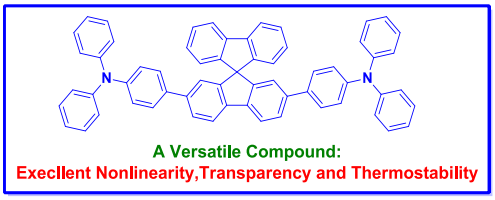
Hongyao Yin [a], Haibo Xiao [a, *], Lei Ding [a], Chun Zhang [b], Aiming Ren [b], Bo Li [c]

[a] Department of Chemistry, Shanghai Normal University, Shanghai 200234, PR China
[b] State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, PR China
[c] Key Laboratory of Polar Materials and Devices, Ministry of Education, East China Normal University, Shanghai 200241, PR China

## HIGHLIGHTS

- We report a molecule exhibiting excellent transparency.
- The two-photon absorption cross-section is as large as 4.5 × $10^3$GM.
- The molecule exhibits excellent thermal stability.
- The molecule is a good two-photon induced blue fluorescent material.
- The spiroconjugation effect explains the excellent properties.

## GRAPHICAL ABSTRACT

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## ABSTRACT

A spirobifluorene-bridged donor/donor chromophore, 2,7-bis-(4-(N,N-diphenylamino)phen-1-yl)-9,9′-spirobifluorene (**SPF-TP**), was found to combine excellent transparency in the near UV–visible region ($\lambda_{cut\text{-}off} \leq 420$ nm), large two-photon absorption cross-section (4.5 × $10^3$GM) and high thermal stability ($T_d$ = 501 °C). In comparison to the reported two-photon absorption molecules, **SPF-TP** represents the best thermal stability so far described in the literature. The main electronic factors explaining the high two-photon absorption activities of **SPF-TP** were analyzed by theoretical calculations. Cyclic voltammograms were employed to explore the causes of the excellent transparency of **SPF-TP**. It was found that the spiroconjugation effect is responsible for the excellent nonlinearity/transparency/thermal stability trade-off in **SPF-TP**. In addition, **SPF-TP** is also a good two-photon induced blue fluorescent material with high fluorescence quantum yield ($\Phi$ = 0.90, in THF).



## 1. Introduction

Two-photon absorption (TPA) has important advantages over conventional one-photon absorption, which has led to applications in microscopy, microfabrication, threedimensional data storage, optical power limiting, upconverted lasing, photodynamic therapy, and for the localized release of bio-active species [1–5]. These applications have generated a demand for new dyes with high two photon absorption cross-sections. The strategies for the design of molecules with large TPA cross-sections have been investigated both theoretically and experimentally [1,2,6] and the results revealed that the TPA cross-section of a molecule depends strongly on the length of its conjugated π system, the strength of electron donating and/or accepting ability, and the planarity of the π-center.

* Corresponding author.
*E-mail address:* xiaohb@shnu.edu.cn (H. Xiao).

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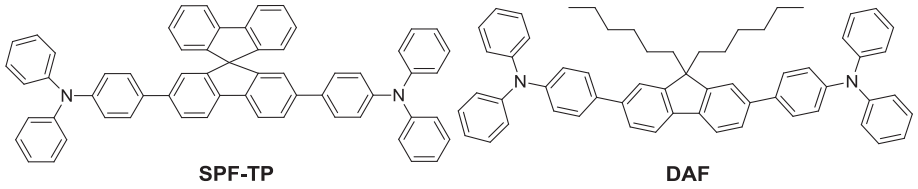


**Scheme 1.** Molecular structures of **SPF-TP** and **DAF**.

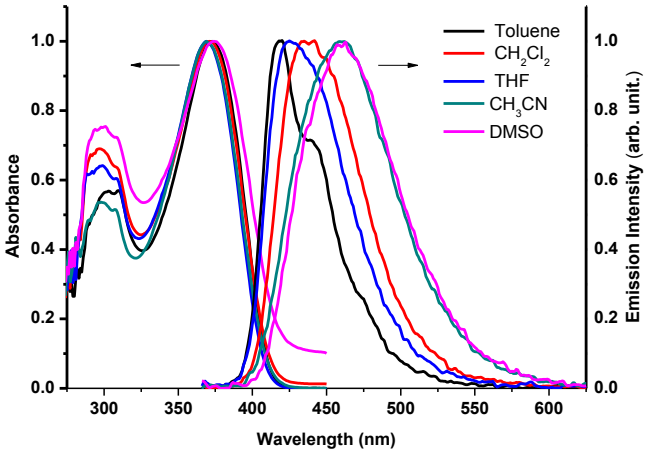


**Fig. 1.** One-photon absorption and fluorescence spectra of **SPF-TP** in solvents of different polarity ($10^{-5}$ M).

Considering the practical applications, the two-photon chromophores have to satisfy additional requirements besides enhanced TPA. For instance, all-optical switching and optical power limiting materials call for chromophores combining superb linear transparency, large optical nonlinearity and high thermal stability [7,8]. Many organic molecules containing extensively delocalized π systems possess large optical nonlinearities [9]. However, these materials also have drawbacks such as non-ideal spectral characteristics and thermal instability. The two-photon absorption property/transparency/thermal stability trade-off still limits the practical applications of two-photon absorption materials in photonics [3,10,11]. In addition, organic two-photon induced fluorescent (TPIF) materials have been widely studied due to their various applications, especially in TPIF microscopy [12,13]. For the probing of natural molecules, efficient TPIF molecules with different emission wavelengths are necessary. So far, the study of TPIF molecules with efficient blue emission is still lacking, which blocks the development of multi-channel TPIF microscopy [14,15].

Herein, we report a spirobifluorene-bridged donor/donor chromophore, 2,7-bis-(4-(N,N-diphenylamino)phen-1-yl)-9,9′-spirobifluorene (**SPF-TP**, Scheme 1), which displays both excellent nonlinearity/transparency/thermal stability trade-off and strong two-photon induced blue fluorescence. The main factors explaining the excellent performances of **SPF-TP** were analyzed. We emphasize that although **SPF-TP** has been synthesized and employed as optoelectronic materials by several groups [16–19], the potentiality of **SPF-TP** for two-photon absorption material has not been considered yet. For the purpose of comparison, compound 2,7 -bis(4-diphenylaminophenyl)-9,9-bis-n-hexylfluorene (**DAF**, Scheme 1) has been chosen as the reference compound in this work [20].

## 2. Experimental

**SPF-TP** was prepared according to the literature method [18]. Steady-state emission and excitation spectra were recorded on Perkin Elmer LS55 instrument. Visible absorption spectra were determined on Perkin Elmer Lambda 35 spectrophotometer. TGA/DTA measurements were performed at heating rate of 10 °C $min^{-1}$ in the temperature range of 25–800 °C, under nitrogen flow of 10 mL $min^{-1}$ by instrument Shimadzu DT-40. Approximately 6 mg of sample were placed in standard aluminum crucible (40 μL). Electrochemical redox potentials were obtained by cyclic voltammetry (CV) using a three-electrode cell and an electrochemistry workstation (CHI830B, Chenhua Shanghai). The working electrode was a Pt ring electrode, the auxiliary electrode was a Pt wire, and saturated calomel electrode (SCE) was used as reference electrode. Tetrabutylammonium perchlorate ($Bu_4NClO_4$) 0.1 M was used as supporting electrolyte in dry $CH_2Cl_2$. Two-photon absorption cross ($\sigma$) of **SPF-TP** was measured by the two photonexcited fluorescence (TPEF) technique using a Ti:Sapphire laser (Spectra-Physics). This laser provided pulses of 100 fs of duration at a repetition rate of 80 MHz and was tunable in the wavelength range of 720–760 nm. The laser beam was focused into a quartz cell of 1 cm path length by using a 5 cm focal-length lens. A half-wave plate and a polarizer were used to control the excitation intensity. The induced two-photon fluorescence was collimated by a lens at a direction perpendicular to the pump beam. To minimize the attenuation of fluorescence due to linear absorption effects, the excitation beam was focused as close as possible to the lateral wall of the quartz cell. The TPEF was then focused into the input slit of an imaging spectrograph and recorded at the exit with a CCD camera. To calculate the TPEF cross sections, Rhodamine B in methanol solution (10 μM) was utilized as references for the calculation. All the samples and

**Table 1**
The HOMO and LUMO energy levels and UV–vis spectra of **SPF-TP** and **DAF** were calculated by DFT/PBE1PBE/6-31G* methods.

| Compd | Gas phase | | | | | In $CH_2Cl_2$ | | | | | Exp[c] [nm] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | LUMO [ev] | HOMO [ev] | △E[a] [ev] | λ [nm] | $f$[b] | LUMO [ev] | HOMO [ev] | △E[a] [ev] | λ [nm] | $f$[b] | |
| **SPF-TP** | −1.15 | −4.91 | 3.76 | 299.07 | 0.2846 | −1.36 | −5.17 | 3.81 | 300.15 | 0.3513 | 296 |
| | | | | 378.34 | 1.7124 | | | | 386.49 | 1.8592 | 369 |
| **DAF** | −1.15 | −5.02 | 3.87 | 299.25 | 0.2126 | −1.31 | −5.15 | 3.84 | 300.19 | 0.2743 | 301 |
| | | | | 376.92 | 1.7567 | | | | 383.97 | 1.9276 | 370 |

[a] The HOMO-LUMO gap.
[b] The corresponding oscillator strength.
[c] The experimental data.