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Synthesis, Two-Photon Absorption and Optical Limiting Properties of Multi-branched Styryl Derivatives Based on 1,3,5-Triazine

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Abstract: Five new multi-branched two-photon absorption triazine chromophores (**T1–T5**) with different donor strength, conjugation length, and direction of charge transfer have been designed and synthesized. The one-photon fluorescence, fluorescence quantum yields, and two-photon properties have been investigated. The two-photon absorption (2PA) cross sections measured by the open aperture Z-scan technique were determined to be 447, 854, 1023, 603, and 766 GM for **T1**, **T2**, **T3**, **T4**, and **T5**, respectively. This result indicates that their 2PA cross section values (σ) increase with increasing electron-donating strength of the end

group, extending the conjugation length of the system, and introducing electron-withdrawing perfluoroalkyl as side groups to the end donor. In addition, the σ value of **T5** is also larger than that of **T1**, which provides evidence that the σ value is relative to the direction of charge transfer (from the ends to the center of the molecule or from the center to the ends). Moreover, significant enhancement of the

two-photon absorption cross section was achieved by introducing a thiophene moiety to a conjugated C=C bond. At the same time, the optical limiting behavior for these chromophores was studied by using a focused 800 nm laser beam with pulses of 140 fs duration. It was found that these molecules also exhibit good optical limiting properties. These initial results clearly demonstrate that multi-branched triazine chromophores are a highly suitable class of two-photon absorbing materials.

Keywords: donor–acceptor systems • multi-branched triazine • optical limiters • perfluoroalkyl • two-photon absorption

Introduction

The promising applications of organic two-photon absorption (2PA) materials in optical limiting, up-converted lasing, microfabrication, 3D optical data storage, bioimaging, and photodynamic therapy^[1] have attracted considerable attention in the last decade. The applications of 2PA materials stimulated substantial research on structure–property rela-

tionships.^[2] The significant issue is how to synthesize the materials with large 2PA cross section. Some efficient molecular design strategies were put forward to provide guidelines for the development of materials with large two-photon absorption cross sections (σ), including donor–acceptor–donor (D–A–D)-type molecules, donor– π -bridge–acceptor (D– π –A)-type molecules, donor– π -bridge–donor (D– π –D)-type molecules, macrocycles, dendrimers, polymers, and multi-branched molecules. These studies reveal that extending the molecular conjugated system for charge transfer or incorporating multi-dipole or quadrupole chromophores into a molecular structure will increase the σ value of a compound while retaining the linear transparency over wide spectral range.^[3] Also, this is a beneficial feature especially for the broadband optical limiting applications based on 2PA. Optical limiting is a significant area to protect human eyes and delicate optical instruments from intense laser beams. An ideal optical limiting material should strongly attenuate intense and potentially dangerous laser beams, while exhibiting high transmittance for low intensity ambient light. Up to now, a number of organic materials have been found to ex-

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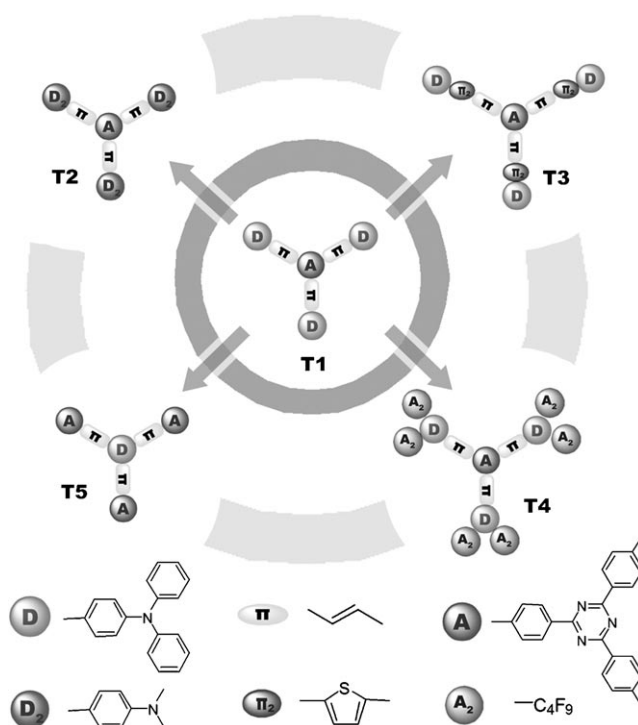
hibit large 2PA cross section and excellent optical limiting properties.^[4] Thus, new compounds with strong two-photon activities are crucially desired in order to realize full potential applications.

Triphenylamine has been widely used in opto- and electro-active materials for its good electron donating and transporting capability, as well as its special propeller starburst molecular structure.^[5] *N,N*-dimethylbenzenamine can enhance the extent of electron delocalization and ability to donate electrons of the 2PA compound. Structurally, the thienyl group has richer π -electron density than the phenyl group and higher chemical and thermal stability than the furan or pyrrole groups, so the introduction of a thiophene moiety was expected to enrich the π -electron density of the system and improve the optoelectronic properties. It is well-known that perfluoroalkyl groups of a strongly electron-withdrawing nature can significantly decrease the energy level of the lowest unoccupied molecular orbital (LUMO), which enhances the materials' electron-accepting ability. Also strong hydrophobic perfluoroalkyl groups lead to an extended charge separation, in which large two-photon absorption cross-sections have often been associated with the extent of conjugation length. However, to the best of our knowledge, only a few examples of perfluoroalkyl substituted 2PA compounds have been reported in the past few years.^[6] On the other hand, 1,3,5-triazine-based compounds show good optical and electrical properties owing to their high electron affinity and symmetrical structure. In particular, octupolar molecules consisting of a strong triazine electron-accepting center and an electron-donating end group linked through a π -conjugated bridge have been shown to be excellent TPA materials.^[7] In our previous work, we studied multibranch triarylamine end-capped triazines with large two-photon absorption cross-sections.^[8] To enrich the research field of triarylamine derivatives with triazine acceptor and to gain more information about their structure-property relationships, in this work, we have synthesized a series of octupolar triazine molecules (**T1–T5**, Scheme 1) containing multibranch styryl derivative moieties and investigated their optical properties.

Results and Discussion

Synthesis

The targeted compounds (**T1–T5**) were synthesized according to Scheme 2. Bromination of 2,4,6-tri(*p*-tolyl)-1,3,5-triazine afforded 2,4,6-tris(4-(bromomethyl)phenyl)-1,3,5-triazine, followed by reaction with trimethyl phosphate, yielding triazine derivative **1**.^[8] The important aldehyde **3** containing perfluoroalkyl unit was synthesized similar to reported literature.^[9] The intermediate aldehyde **4** was synthesized efficiently by Suzuki coupling reactions between 4-bromo-*N,N*-diphenylamine and 5-formylthiophen-2-ylboronic acid.^[10] Finally, condensation of the respective aldehyde, 4-(*N,N*-diphenylamino)benzaldehyde, 4-(dimethylamino)benzaldehyde, **3**, and **4** with triazine moiety (**1**) by the Horner–Wads-



Scheme 1. Structures of multibranch-triazine-based compounds (**T1–T5**).

worth–Emmons reaction gave the target compounds (**T1–T4**). Similarly, **T5** was achieved by the condensation reaction of 4,4',4''-nitrilotribenzaldehyde and dimethyl 4-(4,6-di(*p*-tolyl)-1,3,5-triazin-2-yl) benzylphosphonate (**5**). The final compounds were purified by column chromatography and recrystallization and characterized by ¹H NMR, ¹³C NMR, and HRMS, and they were obtained selectively as their *E*-isomers as shown by the ³*J*_{H–H} coupling constant of approximately 16.0 Hz between all vinylic protons.

One-Photon Absorption and Emission Properties

The UV/Vis absorption spectra of target compounds (**T1–T5**) in CHCl₃ at dilute concentration are shown in Figure 1.

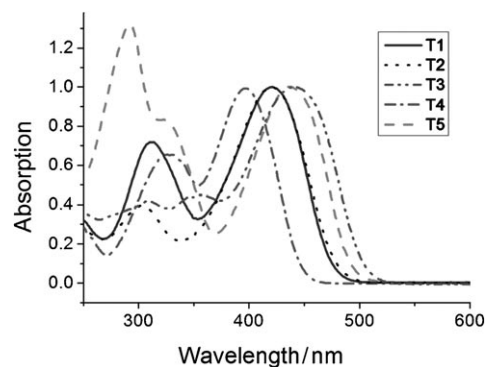
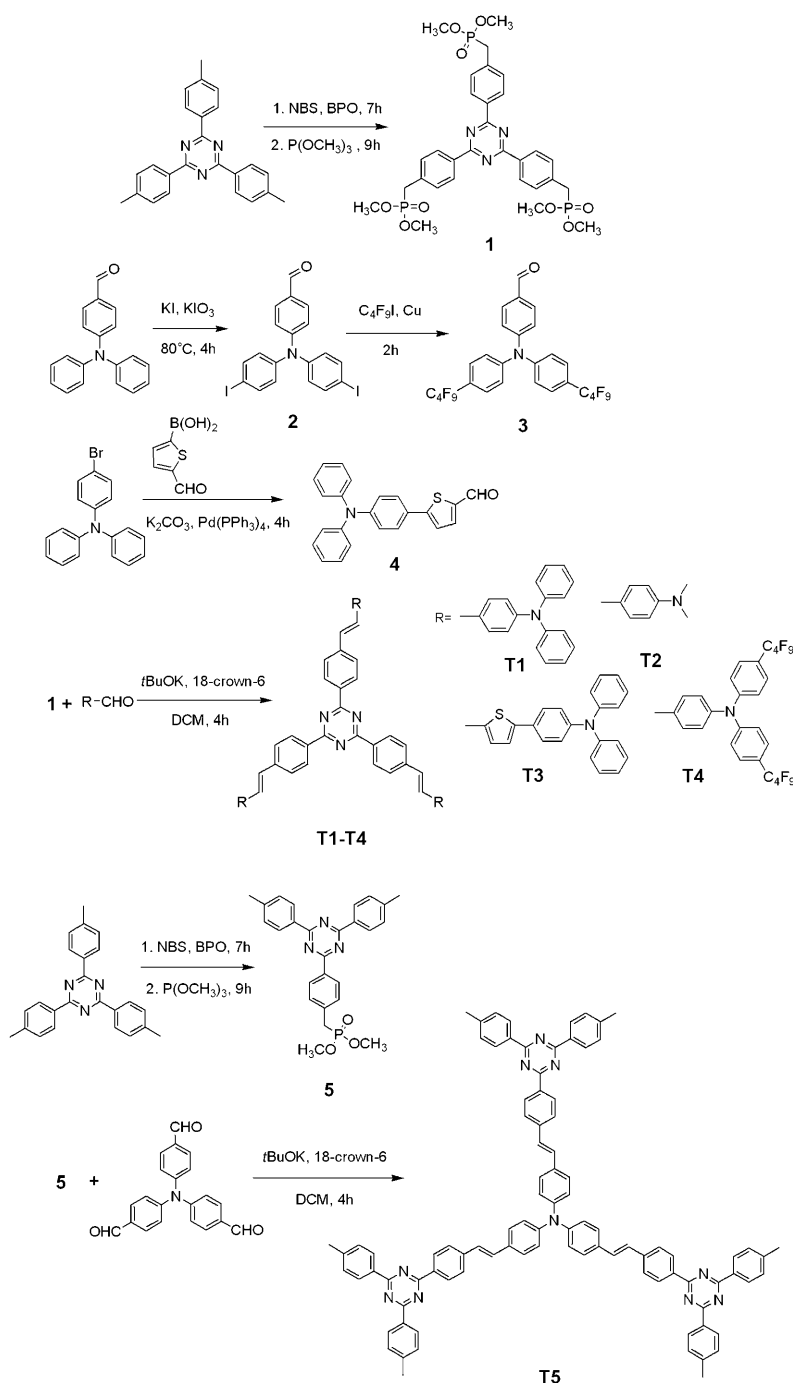


Figure 1. Normalized one-photon absorption spectra of target compounds in CHCl₃.

Scheme 2. Synthetic routes to target compounds **T1–T5**.

The corresponding data are presented in Table 1. All of the compounds show their absorption maximum in the range of 370–450 nm as a result of π – π^* transitions with the order (**T3** > **T5** > **T2** = **T1** > **T4**). In general, the extension of the π -systems exerts an important influence on the absorption spectra. For example, the absorption maximum of **T3** at 441 nm is red-shifted by 20 nm relative to that of **T1**, as **T3** containing a thiophene moiety has a larger conjugation length than **T1**. In addition, for some other compounds with the same electron-donating and electron-accepting group

connected by a different mode (such as **T5** and **T1**), they show two major prominent bands, appearing at 280–350 nm and at 400–480 nm, respectively. The former is ascribed to a localized multi-triazine aromatic π – π^* transition and the latter is of charge-transfer character, in which the absorption maximum of **T5** at 437 nm is red-shifted by 16 nm compared with that of **T1** at 421 nm. It should be noted that **T2** exhibits the same absorption maximum at 421 nm as **T1**, although **T1** has the stronger electron-donating group of *N,N*-dimethylaniline. This suggests that their UV/Vis absorption was not only attributed to a strong ICT effect but also the delocalization of intra-molecular charge in the system. Comparing the single-photon absorption maximum of **T1**, **T4** is blue-shifted with increasing electron-withdrawing perfluoroalkyl as side groups to the end triphenylamine donor, in which a stronger electron acceptor would help to stabilize the charge-separated excited state of the molecule.

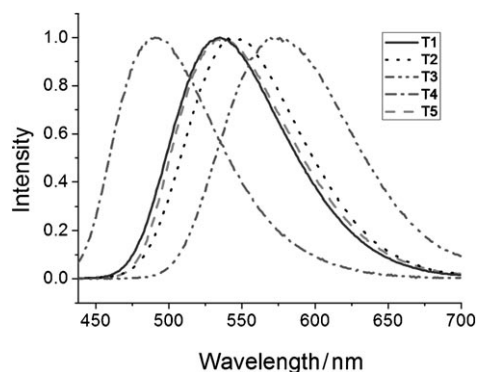
One-photon excited fluorescence spectra for these compounds were recorded on a Varian Cary Eclipse fluorescence spectrophotometer using dilute chloroform solutions and the data are summarized in Table 1. All the compounds have strong one-photon fluorescence. As shown in Figure 2, **T1–T5** show an emission maximum at 535, 544, 575, 490, and 536 nm, respectively, whereby the Stokes shifts vary from 4226

to 5370 cm^{-1} , which are also in agreement with the order of the extension of the π -systems and the increase of electron-donating ability of the donors: *N,N*-dimethylaniline > triphenylamine > *N,N*-bis(4-(perfluorobutyl)phenyl)aniline. Different from UV/Vis absorption, **T2** shows a more red-shifted maximum emission than **T1** as a result of the stronger *N,N*-dimethylaniline electron-donating ability, while **T5** and **T1** exhibits nearly the same emission maximum (e.g., **T5**, 436 nm; **T1**, 435 nm) owing to their same donor and acceptor. The fluorescence quantum yields (Φ_f) of these molecules

Table 1. One-photon and two-photon properties of **T1–T5**.

	T1	T2	T3	T4	T5
$\lambda_{\text{abs,max}}$ [nm]	421	421	441	395	437
$\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$	12.71	10.21	13.16	15.01	9.95
$\lambda_{\text{em,max}}$ [nm]	535	544	575	490	536
$\Phi_f^{[a]}$	0.27	0.37	0.25	0.86	0.32
τ [ns] ^[b]	2.16	2.22	2.06	1.83	2.23
K_r [10^8 s^{-1}] ^[c]	1.25	1.66	1.21	4.69	1.43
K_{nr} [10^8 s^{-1}] ^[c]	3.38	2.84	3.64	0.77	3.05
$\sigma_{\text{TPA}}(\text{GM})^{[d]}$	447	854	1023	603	766
$\lambda_{\text{TPF}}(\text{nm})^{[e]}$	545	555	580	510	542

[a] The PL quantum yield (Φ_f) was estimated with rhodamine B in ethanol as a standard. [b] fluorescence lifetime (τ). [c] Rate constants for radiative (k_r) and nonradiative (k_{nr}) decay. [d] Two-photon absorption (TPA) cross section excited at 800 nm (140 fs) in $10^{-50} \text{ cm}^4 \text{ s}$ per photon (GM). [e] The maximum two-photon fluorescence (TPF) excited at 800 nm.

Figure 2. Normalized one-photon emission spectra of target compounds in CHCl_3 .

were measured with reference to rhodamine B in ethanol and listed in Table 1. Interestingly, the Φ_f value of **T4** is very high (86%), suggesting that the flexible perfluorohexyl chains not only function as solubilizing groups but also help suppress the nonradiative decay pathways. In order to confirm the comment, we have measured the fluorescence lifetime (τ) and determined the decay rate constants, in which the rate constants for radiative (k_r) and nonradiative (k_{nr}) decays can be estimated from the fluorescence quantum yields and lifetimes^[11] using Equations (1) and (2) and are included in Table 1:

$$\Phi_f = \frac{K_r}{K_r + K_{nr}} \quad (1)$$

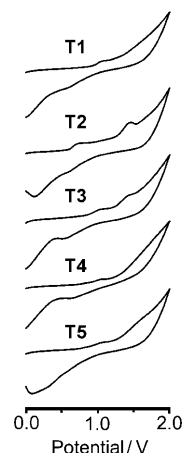
and

$$\tau = (K_r + K_{nr})^{-1} \quad (2)$$

The value of k_{nr} for molecule **T4** is lower than those of the other compounds. The emission spectra for **T4** exhibits a blue shift with the introduction of electron-withdrawing perfluorohexyl chains, implying that the energy gap between ground and excited states increases and electron recombination of the two states is more difficult. Thus **T4** shows a relatively low k_{nr} value.

Electrochemical Properties

Figure 3 shows the cyclic voltammetry (CV) diagrams of the compounds using 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte in THF solution with

Figure 3. Cyclic voltammograms of **T1–T5** in THF containing 0.1 mol L^{−1} of tetrabutylammonium hexafluorophosphate (TBAPF₆).

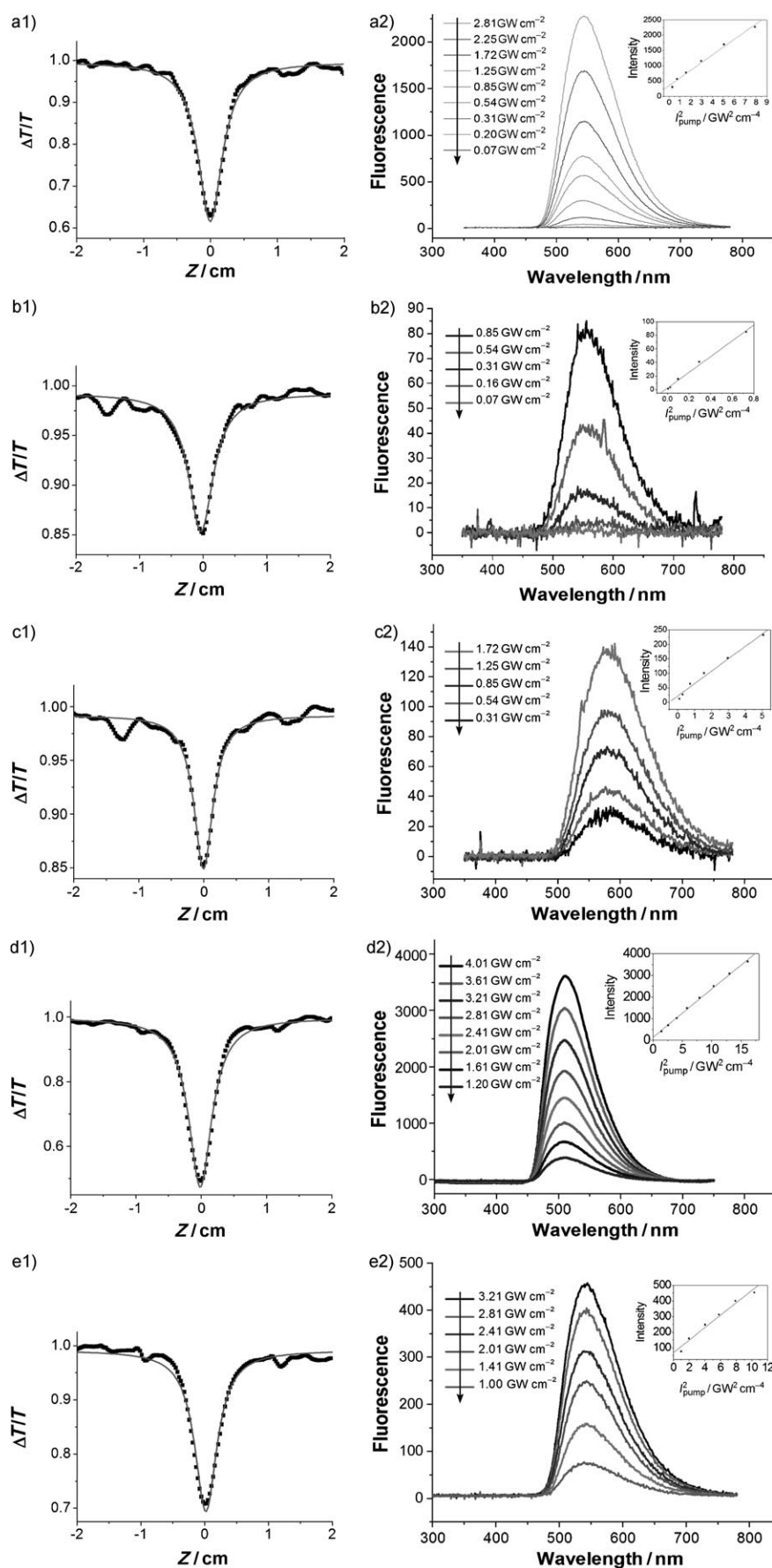
platinum button working electrodes, a platinum wire counter electrode, and an SCE reference electrode. The SCE reference electrode was calibrated using a ferrocene/ferrocenium (Fc/Fc^+) redox couple as an external standard. The electrochemical properties as well as the energy level parameters of **T1–T5** are listed in Table 2. It can be observed from

Table 2. Electrochemical properties of **T1–T5**.

Compound	$E_{\text{HOMO}}^{[a]}$ [eV]	$E_{0-0}^{[b]}$ [eV]	$E_{\text{LUMO}}^{[c]}$ [eV]
T1	−5.54	2.61	−2.93
T2	−5.34	2.58	−2.76
T3	−5.50	2.46	−3.04
T4	−5.61	2.80	−2.81
T5	−5.63	2.56	−3.07

[a] E_{HOMO} were measured in THF with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as electrolyte (working electrode: Pt; reference electrode: SCE; calibrated with ferrocene/ferrocenium (Fc/Fc^+) as an external reference. Counter electrode: Pt wire). [b] E_{0-0} was estimated from the intercept of the normalized absorption and emission spectra. [c] E_{LUMO} is estimated by subtracting E_{0-0} to HOMO.

Figure 3 that the first half-wave potentials (E_{ox}) of **T1–T5** were 0.84, 0.64, 0.80, 0.91, and 0.93 V, respectively. Therefore, the ground state oxidation potential corresponding to the HOMO energy levels are −5.54, −5.34, −5.50, −5.61, and −5.63 (vs vacuum), respectively, according to the equation $\text{HOMO} = -e(E_{\text{ox}} + 4.7)$ (eV).^[12] It is clear that the HOMO levels of **T2** are higher than other compounds, which is caused by the stronger electron-donating ability of *N,N*-dimethylaniline. **T1** and **T3** showed a similar HOMO energy level owing to their identical donor and acceptor. However, **T4** and **T5**, containing electron-withdrawing per-



fluoroalkyl and three triazine moieties, respectively, possessed relatively low HOMO energy levels. Generally, the stronger electron-donating ability of the donor resulted in a higher HOMO energy level. On the other hand, the introduction of three triazine groups into **T5** lowers the LUMO energy level of the compound by increasing the electron affinity.

Two-Photon Absorption Properties

2PA cross sections of the **T1**–**T5** were determined by the femto-second open aperture Z-scan technique according to a previously described method.^[13] Figure 4a1–e1 shows the open-aperture Z-scan data of **T1**–**T5**, and the 2PA coefficient is obtained by fitting of the data. The 2PA cross section (σ) can be calculated by using the equation $\sigma = h\nu\beta/N_0$, where $N_0 = N_A C$ is the number density of the absorption centers, N_A is the Avogadro constant and C represents the solute molar concentration. The values of σ for **T1**–**T5** are 447, 854, 1203, 607, and 766 GM at 800 nm, respectively (Table 1). The 2PA cross section of **T2** (854 GM) is larger than **T1** (447 GM), because the *N,N*-dimethylaniline groups in compound **T2** have a stronger electron-donating ability compared with the triphenylamine group in **T1**. It is well-known that a higher strength electron acceptor/donor will cause a greater degree of charge transfer in

Figure 4. (a1–e1) Open aperture Z-scan results for **T1**–**T5** solutions in CHCl_3 , respectively, using 800 nm fs pulses (scattered circle experimental data, straight line theoretic fitted data). (a2–e2) TPF intensities of compound **T1**–**T5** under different excitation power density, respectively. Inset is TPF intensity versus the square of the excitation power density.

donor–acceptor systems, resulting in a higher nonlinear optical response.^[14] The larger 2PA cross section of **T3** (1023 GM) arises from the introduction of a thiophene group in the π bridge, which extends the conjugate system by importing hetero atoms. Interestingly, the σ value of **T4** is higher than that of **T1**, suggesting that the magnitude of σ can thus be controlled through the modification of the molecular structure in such a way as to affect the amount of intramolecular charge transfer. In addition, the σ value of **T5** is also larger than that of **T1**, which provides evidence that the σ value is relative to the direction of charge transfer (from the ends to the center of the molecule or from the center to the ends). These results show that the strategy through increasing electron-donating strength of the end group, extending the conjugation length of the system, introducing electron-withdrawing perfluoroalkyl as side groups to the end donor, and changing the direction of charge transfer are effective approaches for enhancing 2PA cross section of styryl derivatives-1,3,5-triazine-based star-shaped molecules. Moreover, among these approaches, extending the conjugation length by addition of a heterocycle is the most effective way to increase the σ value.

Under the excitation of 140 fs, 800 nm pulses, target compounds in CHCl_3 emit intense frequency up-converted fluorescence with the maxima located in the range from 510 to 580 nm. (Table 1) The fluorescence could even be seen by the naked eye under excitation of unfocused laser pulses with energy of several μJ . The two-photon fluorescence spectrum of the compounds **T1–T5** under different laser intensity is shown in Figure 4(a2–e2). The linear dependence of fluorescence intensity on the square of the excitation intensity, as shown in the inset, confirms that 2PA is the main excitation mechanism of the intense fluorescence emission. Intense two-photon fluorescence was even observed at an excitation intensity of about 1 GW cm^{-2} (**T4**), indicating the large 2PA cross section and high two-photon fluorescence quantum yields. This is an important prerequisite for 2PA-based applications such as fluorescence microscopy and up-converted lasing. It should be noted that for the compounds **T1–T5**, the two-photon excitation studies were performed at one wavelength (800 nm), which is closer to the 2-fold $\lambda_{\text{abs,max}}$ of **T4**. We can not measure the 2PA cross section profile at different wavelengths at present because of the limit of our laser apparatus. The cross sections for the other compounds would be better conducted at their relative 2-fold $\lambda_{\text{abs,max}}$.

2PA-based Optical Limiting Properties

For some laser-based applications, such as optical communication, optical fabrication, and manufacturing, the intensity or energy stability of the utilized laser beam is important. This is because random intensity or power fluctuations may be troublesome, especially from the standpoint of reproducibility, for these applications. However, a strongly multi-photon absorbing medium could be one of the approaches used to reduce such fluctuation and stabilize the pulsed laser signals.^[28] Since these chromophores have relatively

large 2PA at 800 nm, we investigated the relationship between the output intensity and the input intensity using these five chromophores. The optical limiting properties of five compounds, at concentrations of $0.0052 \text{ mol L}^{-1}$, $0.00085 \text{ mol L}^{-1}$, $0.00055 \text{ mol L}^{-1}$, $0.0064 \text{ mol L}^{-1}$, and $0.0021 \text{ mol L}^{-1}$ for **T1–T5**, respectively, dissolved in CHCl_3 solutions, were investigated by using the open-aperture Z-scan technique, with 800 nm laser pulses of 140 fs pulse duration. The measured relationships between the incident and output fluence for these compounds are shown in Figure 5.

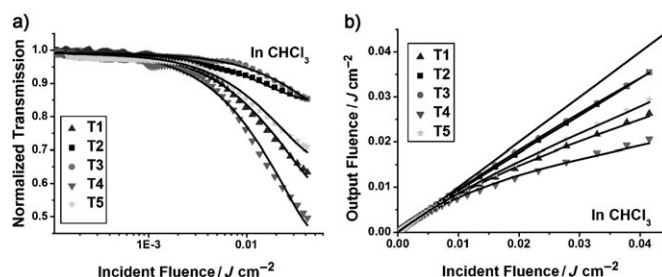


Figure 5. Measured output intensity versus input intensity of the 800 nm laser pulses based on chromophores **T1–T5**; The points are the experimental data, while the solid lines are the theoretical fits.

All these five compounds are shown to exhibit an optical limiting behavior. At low incident energy, all five compounds show a linear response of transmitted energy in accordance with Beer's law, but the transmission deviates significantly from linearity as the incident fluence increases. We chose a power to carry out the measurement at which pure CHCl_3 solvent shows no detectable optical limiting behavior, indicating that the solvent contribution is negligible, so the observed optical limiting properties can be assigned solely to the compounds. Besides, it should be noted that the concentrations in our measurements are relatively low owing to the limit of solubility; hence, lower threshold values could be attained if higher concentrations are used or the compounds are deposited as thin films.

From the characteristic curves in Figure 5, one can see why a two-photon absorbing medium can be used to stabilize the laser pulse fluctuation. When the incident fluence increase from $\sim 0.0010 \text{ J cm}^{-2}$ to $\sim 0.042 \text{ J cm}^{-2}$ (an increase of about 42 times), the transmitted output fluences only show 20-fold, 25-fold, 29-fold, 35-fold, and 35-fold increase for compound **T4**, **T1**, **T5**, **T2**, and **T3**, respectively, which fits the theoretically predicted optical limiting behavior (solid lines) based on the 2PA. These results suggest that this series of multi-branched compounds would provide attractive potential in the optical limiting field owing to an enhanced two-photon response.

Conclusions

In conclusion, a series of new multi-branched triazine chromophores containing styryl derivatives have been synthe-

sized and characterized. Their linear and nonlinear optical properties were investigated. One-photon absorption and emission spectra revealed that the Stokes shifts for these chromophores increased with an increasing extension of the π -systems and increase of electron-donating ability of the donors, whereas the fluorescence quantum yield exhibited large increases with the introduction of electron-accepting perfluoroalkyl as side groups to the end donor. Investigation of the 2PA properties of these chromophores reveals that their 2PA cross section values increase with increasing electron-donating strength of the end group, extending the conjugation length of the system, introducing electron-accepting perfluoroalkyl, and making charge transfer from the center of the triphenylamine to the triazine ends possible. In conjunction with the increased fluorescence quantum yield, we believe that the multi-branched triazine chromophore with perfluoroalkyl moiety will provide a potential application in two-photon fluorescence bioimaging. These molecules also exhibit good optical limiting properties and make them potential candidates for optical limiters in the photonics field.

Experiment Section

Materials and Methods

Tetrahydrofuran (THF) was pre-dried over 4 Å molecular sieves and distilled under argon atmosphere from sodium benzophenone ketyl immediately prior to use. Triethylamine was distilled under normal pressure and dried over potassium hydroxide. *N,N*-dimethyl formamide (DMF) and dichloromethane (DCM) were refluxed with calcium hydride and distilled before used. Starting materials 2,4,6-tri(*p*-tolyl)-1,3,5-triazine and 4-bromo-*N,N*-diphenyl-benzenamine were prepared according to published procedures.^[7c,10] All other chemicals were purchased from Aldrich and used as received without further purification.

Instrumentation

¹H and ¹³C NMR spectra were recorded on a Bruker AM-400 spectrometer using [D]chloroform as solvent and tetramethylsilane ($\delta=0$) as internal reference. The UV/Vis spectra were recorded on a Varian Cary 500 spectrophotometer with 2 nm resolution at room temperature. The fluorescence spectra were taken on a Varian Cary fluorescence spectrophotometer. The cyclic voltammograms of compounds were obtained with a Versastat II electrochemical workstation (Princeton applied research) using a normal three-electrode cell with a Pt working electrode, a Pt wire counter electrode, and saturated calomel electrode (SCE) reference electrode in saturated KCl solution. TPA cross sections of **T1–T5** were measured by femtosecond open-aperture Z-scan technique according to the previously described method.^[12] Two-photon excited fluorescence (TPF) was excited by femtosecond pulses with different intensities at a wavelength of 800 nm. The repetition rate of the laser pulses is 1 kHz and the pulse duration is 140 fs.

Synthesis

(4,4',4''-(1,3,5-Triazine-2,4,6-triyl)tris(benzene-4,1-diyl))tris(methylene)triphosphonate (1). In a 100 mL round-bottom flask, 2,4,6-tri(*p*-tolyl)-1,3,5-triazine (3.51 g, 0.01 mol), *N*-bromosuccinimide (NBS) (5.34 g, 0.03 mol), and benzoyl peroxide (BPO) (0.3 g, 1.2 mmol) were dissolved into chlorobenzene (50 mL) and heated at 110 °C for 7 h. The mixture was filtered and the solvent was removed using a rotary evaporator. The residue was dissolved into trimethyl phosphite (10 mL) and refluxed for 9 h. The excessive trimethyl phosphite was removed under vacuum. The residue was purified by column chromatography on silica (ethanol/dichloromethane = 1:10, v/v) to afford the product as a white powder (5.3 g, yield: 78 %).

¹H NMR (CDCl₃, 400 MHz, TMS): $\delta=8.71$ (d, 6H, $J=8.0$ Hz), 7.51 (m, 6H), 3.61 (d, 18H, $J=10.8$ Hz), 3.30 ppm (d, 6H, $J=22.0$ Hz); ¹³C NMR (CDCl₃, 100 MHz, TMS): $\delta=171.3$, 136.3, 136.2, 135.0, 135.0, 130.1, 130.1, 129.3, 129.2, 53.1, 53.0, 33.9, 32.5 ppm; HRMS (EI) (m/z) calcd for C₃₀H₃₆N₃O₉P₃: 675.1664 [M]; found: 675.1663.

4-[*N,N*-Bis(4-iodophenyl)amino]benzaldehyde (2). A modified version of a previously reported method^[8] was used. In a 500 mL three-necked round-bottom flask, 4-(*N,N*-diphenylamino)benzaldehyde (14.00 g, 51.28 mmol), potassium iodide (11.43 g, 68.85 mmol), acetic acid (210 mL), and water (20 mL) were heated to 80 °C. After stirring for 1 h, potassium iodate (10.97 g, 51.26 mmol) was added and the reaction was stirred at 80 °C for 4 h. The solution was allowed to cool and the solid was collected, washed with water, and recrystallized from DCM/ethanol (1:5) giving the product as a yellow powder (20.05 g, 75 %). ¹H NMR (CDCl₃, 400 MHz, TMS): $\delta=9.89$ (s, 1H), 7.75 (d, 2H, $J=9.0$ Hz), 7.67 (d, 4H, $J=9.0$ Hz), 7.09 (d, 2H, $J=9.0$ Hz), 6.93 ppm (d, 4H, $J=9.0$ Hz); MS(EI) (m/z) calcd for C₁₉H₁₃I₂NO: 524.9 [M]; found: 525.2.

4-(bis(4-(perfluorobutyl)phenyl)amino)benzaldehyde (3). In a 100 mL three-necked round-bottom flask, **2** (1.05 g, 2 mmol), copper powder (3.64 g, 56.8 mmol), and 20 mL DMF were heated to 125 °C under an argon atmosphere. Then, perfluorobutyl iodide (4.43 g, 12.8 mmol) was added and the reaction was stirred at 125 °C for 2 h. The reaction was stopped by adding water (20 mL). The mixture was filtered and washed with water and ether. The combined organic phases were dried over anhydrous MgSO₄ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (petroleum ether/dichloromethane = 2:1, v/v) to yield the product as a yellow powder (850 mg, yield: 60 %). ¹H NMR (CDCl₃, 400 MHz, TMS): $\delta=9.93$ (s, 1H), 7.82 (d, 2H, $J=8.4$ Hz), 7.54 (d, 4H, $J=8.4$ Hz), 7.25 (d, 4H, $J=8.4$ Hz), 7.19 ppm (d, 2H, $J=8.4$ Hz); ¹³C NMR (CDCl₃, 100 MHz, TMS): $\delta=190.5$, 151.6, 149.3, 132.0, 131.5, 128.6, 124.9, 124.7, 123.3 ppm; ¹⁹F NMR (CDCl₃, 376 MHz, TMS): $\delta=-81.89$ (t, 18F, $J=-7.52$ Hz), -111.48 (t, 12F, $J=-11.28$ Hz), -123.55 (d, 12F, $J=-7.52$ Hz), -126.50 ppm (t, 12F, $J=-11.28$ Hz); MS (EI) (m/z) calcd for C₂₇H₁₃F₁₈NO: 709.1 [M]; found: 709.1.

5-(4-(diphenylamino)phenyl)thiophene-2-carbaldehyde (4). In a 100 mL three-necked round-bottom flask, 4-bromo-*N,N*-diphenylaniline (340 mg, 1 mmol), K₂CO₃ (1.38 g, 10 mmol), Pd(PPh₃)₄ (50 mg, 0.05 mmol), water (5 mL), and THF (15 mL) were heated to 45 °C for 1 h under an argon atmosphere. Then, 5-formylthiophen-2-ylboronic acid (187 mg, 1.2 mmol) dissolved in 5 mL THF was added and the reaction was stirred at 45 °C for 4 h. The mixture was washed with water and chloroform. The combined organic layer was dried over anhydrous MgSO₄ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (petroleum ether/dichloromethane = 1:1, v/v) to yield the product as a yellow powder (300 mg, yield: 42 %). ¹H NMR (400 MHz, CDCl₃): $\delta=9.85$ (s, 1H), 7.72 (d, 1H, $J=4.00$ Hz), 7.61 (d, 2H, $J=8.40$ Hz), 7.52 (d, 1H, $J=4.00$ Hz), 7.27–7.31 (m, 4H), 7.10–7.16 (m, 6H), 6.89 ppm (d, 2H, $J=8.40$ Hz).

4,4',4''-2,2',2''-(4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(benzene-4,1-diyl))tris(ethene-2,1-diyl)tris(*N,N*-diphenylaniline) (T1). In a 100 mL three-necked round-bottom flask, **1** (267 mg, 0.35 mmol), 4-(diphenylamino)benzaldehyde (288 mg, 1.05 mmol), *t*BuOK (236 mg, 2.1 mmol), and dichloromethane (50 mL) were added and the reaction was stirred at 45 °C for 4 h. The mixture was washed with water and chloroform. The combined organic layers were dried over anhydrous MgSO₄ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (petroleum ether/dichloromethane = 3:1, v/v) to yield the product as a yellow powder (160 mg, yield: 40 %). ¹H NMR (CDCl₃, 400 MHz, TMS): $\delta=8.72$ (d, 6H, $J=8.4$ Hz), 7.69 (d, 6H, $J=8.4$ Hz), 7.45 (d, 6H, $J=8.4$ Hz), 7.29 (d, 3H, $J=16.0$ Hz), 7.28–7.23 (m, 12H), 7.14–7.12 (m, 12H), 7.11 (d, 3H, $J=16.0$ Hz), 7.09–7.03 ppm (m, 12H); ¹³C NMR (CDCl₃, 100 MHz, TMS): $\delta=171.8$, 148.5, 148.1, 142.4, 135.8, 131.7, 130.8, 130.4, 130.0, 128.4, 127.1, 127.0, 125.8, 125.4, 124.0, 123.9, 120.0, 111.4, 100.9 ppm; HRMS (ESI) (m/z) calcd for C₈₁H₆₀N₆: 1117.4957 [M]; found: 1117.5000.

4,4',4''-2,2',2''-(4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(benzene-4,1-diyl))tris(ethene-2,1-diyl)tris(*N,N*-dimethylaniline) (T2). In a 100 mL three-

necked round-bottom flask, **1** (267 mg, 0.35 mmol), 4-(dimethylamino)-benzaldehyde (156 mg, 1.05 mmol), *t*BuOK (236 mg, 2.1 mmol), and dichloromethane (50 mL) were added and the reaction was stirred at 45°C for 4 h. The mixture was washed with water and chloroform. The combined organic layer was dried over anhydrous MgSO₄ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (petroleum ether/dichloromethane = 3:1, v/v) to yield the product as a yellow powder (82 mg, yield: 31%). ¹H NMR (CDCl₃, 400 MHz, TMS): δ = 8.76 (d, 6H, *J* = 8.4 Hz), 7.69 (d, 6H), 7.51 (d, 6H, *J* = 8.8 Hz), 7.26 (d, 3H, *J* = 16.4 Hz), 7.05 (d, 3H, *J* = 16.4 Hz), 6.77 (d, 6H, *J* = 8.8 Hz), 3.04 ppm (s, 18H); ¹³C NMR (CDCl₃, 100 MHz, TMS): δ = 171.8, 151.1, 143.0, 135.3, 131.5, 130.0, 128.6, 126.8, 126.1, 124.4, 113.1, 41.1 ppm; HRMS (ESI) (*m/z*) calcd for C₃₁H₄₈N₆: 744.5402 [*M*]; found: 745.4045.

4,4',4''-(5,5',5''-2,2',2''-(4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(benzene-4,1-diyl))tris(ethene-2,1-diyl))tris(thiophene-5,2-diyl))tris(*N,N*-diphenylamine) (T3). In a 100 mL three-necked round-bottom flask, **1** (267 mg, 0.35 mmol), 5-(4-(diphenylamino)phenyl)thiophene-2-carbaldehyde (373 mg, 1.05 mmol), *t*BuOK (236 mg, 2.1 mmol), and dichloromethane (50 mL) were added and the reaction was stirred at 45°C for 4 h. The mixture was washed with water and chloroform. The combined organic layer was dried over anhydrous MgSO₄ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (petroleum ether/dichloromethane = 3:1, v/v) to yield the product as a yellow powder (204 mg, yield: 43%). ¹H NMR (CDCl₃, 400 MHz, TMS): δ = 8.71 (d, 6H, *J* = 7.4 Hz), 7.63 (d, 6H, *J* = 7.4 Hz), 7.48 (d, 6H, *J* = 7.4 Hz), 7.35 (d, 3H, *J* = 16 Hz), 7.30–7.26 (m, 12H), 7.14–7.05 (m, 30H), 6.98 ppm (d, 3H, *J* = 16 Hz); ¹³C NMR (CDCl₃, 100 MHz, TMS): δ = 171.7, 148.2, 148.1, 144.6, 141.9, 141.8, 135.9, 130.1, 129.2, 128.7, 127.9, 127.7, 127.2, 127.0, 126.3, 125.9, 125.5, 125.4, 124.6, 124.1, 124.0, 123.5 ppm; HRMS (ESI) (*m/z*) calcd for C₉₃H₆₆N₆S₃: 1363.4511 [*M*]; found: 1363.4522.

4,4',4''-2,2',2''-(4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(benzene-4,1-diyl))tris(ethene-2,1-diyl)tris(*N,N*-bis(4-(1,1,3,3,4,4,4-heptafluorobutyl)phenyl)amino)benzaldehyde (T4). In a 100 mL three-necked round-bottom flask, **1** (267 mg, 0.35 mmol), 4-(bis(4-(1,1,3,3,4,4,4-heptafluorobutyl)phenyl) amino)benzaldehyde (668.8 mg, 1.05 mmol), *t*BuOK (236 mg, 2.1 mmol), and dichloromethane (50 mL) were added and the reaction was stirred at 45°C for 4 h. The mixture was washed with water and chloroform. The combined organic layers were dried over anhydrous MgSO₄ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (petroleum ether/dichloromethane = 3:1, v/v) to yield the product as a yellow powder (552 mg, yield: 71%). ¹H NMR (CDCl₃, 400 MHz, TMS): δ = 8.78 (d, 6H, *J* = 8.4 Hz), 7.72 (d, 6H, *J* = 8.4 Hz), 7.57 (d, 6H, *J* = 8.4 Hz), 7.48 (d, 12H, *J* = 8.4 Hz), 7.27 (d, 3H, *J* = 16.4 Hz), 7.21 (d, 12H, *J* = 8.4 Hz), 7.19 (d, 3H, *J* = 16.4 Hz), 7.16 ppm (d, 9H, *J* = 8.4 Hz); ¹³C NMR (CDCl₃, 100 MHz, TMS): δ = 172.8, 151.6, 147.4, 1423.0, 137.2, 135.7, 131.2, 131.1, 129.9, 129.8, 128.4, 127.8, 124.9, 124.7, 124.5, 120.3, 115.4 ppm; ¹⁹F NMR (CDCl₃, 376 MHz, TMS): δ = -81.91 (t, 18F, *J* = -7.52 Hz), -111.26 (t, 12F, *J* = -11.28 Hz), -123.59 (d, 12F, *J* = -7.52 Hz), -126.50 ppm (t, 12F, *J* = -11.28 Hz); HRMALDI-TOF: calcd for C₁₀₅H₅₄F₅₄N₆: 2424.3497 [*M*]; found: 2424.3479.

Dimethyl 4-(4,6-di(*p*-tolyl)-1,3,5-triazin-2-yl)benzylphosphonate (5). In a 100 mL round-bottom flask, 2,4,6-tri(*p*-tolyl)-1,3,5-triazine (3.51 g, 0.01 mol), NBS (1.78 g 0.01 mol), and BPO (0.1 g, 0.4 mmol) were dissolved into chlorobenzene (50 mL) and heated at 110°C for 7 h. The mixture was filtered and the solvent was removed using a rotary evaporator. The residue was dissolved into trimethyl phosphite (10 mL) and refluxed for 9 h. The excessive trimethyl phosphite was removed under vacuum. The residue was purified by column chromatography on silica (petroleum ether/dichloromethane = 1:2, v/v) to afford the product as a white powder (3.8 g, yield: 83%). ¹H NMR (CDCl₃, 400 MHz, TMS): δ = 8.72 (d, 2H, *J* = 7.6 Hz), 8.65 (d, 4H, *J* = 8.4 Hz), 7.50 (d, 2H, *J* = 6 Hz), 7.37 (d, 4H, *J* = 8 Hz), 3.70 (d, 6H, *J* = 10.8 Hz), 3.30 (d, 2H, *J* = 22.0 Hz), 2.48 ppm (s, 6H); ¹³C NMR (CDCl₃, 100 MHz, TMS): δ = 171.5, 143.1, 133.6, 130.1, 130.0, 129.9, 129.2, 128.9, 53.1, 53.0, 33.9, 32.5, 21.8 ppm.

Tris(4-(4-(4,6-di(*p*-tolyl)-1,3,5-triazin-2-yl)styryl)phenyl)amine (T5). In a 100 mL three-necked round-bottom flask, **5** (483 mg, 1.05 mmol), 4,4',4''-

nitrotribenzaldehyde (115 mg, 0.35 mmol), *t*BuOK (236 mg, 2.1 mmol), and 50 mL dichloromethane were added and the reaction was stirred at 45°C for 4 h. The mixture was washed with water and chloroform. The combined organic layer was dried over anhydrous MgSO₄ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (petroleum ether/dichloromethane = 3:1, v/v) to yield the product as a yellow powder (133 mg, yield: 29%). ¹H NMR (CDCl₃, 400 MHz, TMS): δ = 8.75 (d, 6H, *J* = 8.4 Hz), 8.66 (d, 12H, *J* = 8.0 Hz), 7.69 (d, 6H, *J* = 8.4 Hz), 7.52 (d, 6H, *J* = 8.4 Hz), 7.38 (d, 12H, *J* = 8.0 Hz), 7.26 (d, 3H, *J* = 16.0 Hz), 7.17 (d, 6H, *J* = 8.4 Hz), 7.15 (d, 3H, *J* = 16.0 Hz), 2.48 ppm (s, 18H); ¹³C NMR (CDCl₃, 100 MHz, TMS): δ = 172.1, 171.7, 147.6, 143.6, 142.2, 136.0, 134.4, 132.8, 130.6, 130.0, 129.6, 128.5, 127.6, 127.2, 125.0, 22.4 ppm. HRMS (ESI) (*m/z*) calcd for C₉₃H₇₂N₁₀: 1329.6019 [*M*]; found: 1329.5973.

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