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Three Asymmetrical Conjugated D-π-D′ Sulfur-Containing Chromophores with a Focus on Two-Photon Absorption

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Three novel asymmetrical D-π-D′ type sulfur-containing chromophores, (*E*)-4-(4-(benzylthio)styryl)-*N*,*N*-diethylbenzenamine (**S1**), (*E*)-4-(4-(*tert*-butylthio)styryl)-*N*,*N*-diethylbenzenamine (**S2**) and (*E*)-4-(4-(thio)styryl)-*N*,*N*-diethylbenzenamine (**S3**), were synthesized and characterized. Two kinds of substituents and hydrogen were introduced into the three different chromophores to investigate the influence of electron distribution on the sulfur atom. Meanwhile, a simple synthetic strategy of π-conjugated 4-(thio)styrene derivatives was performanced successfully. Linear and non-linear optical properties of **S1**, **S2** and **S3** were investigated both experimentally and theoretically. The optical properties indicate that they all have obvious characteristics of asymmetrical dipole molecules. The measured maximum two-photon cross-sections of **S1**–**3** are 79, 57 and 19 GM (Goeppert-Mayer), respectively. It shows that the different substituents on the sulfur atom in molecules **S1**–**3** lead to different electronic structures, which affect the optical properties. In these structures, the aromatic benzyl substituent (in **S1**) is superior for optimizing two-photon activity in the designed molecular framework.

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Introduction

Two-photon absorption (TPA) is a third-order non-linear optical process and offers outstanding advantages over single-photon absorption.[1] Since the 1990s, it has drawn significant attention owing to its broad potential applications in various fields, such as three-dimensional (3D) optical memory and data storage,[2] 3D optical imaging,[3] 3D lithographic microfabrication,[4] and photodynamic therapy,[5] among many others.[6] As organic synthesis makes it easy to shape and fine-tune molecules into desired structures, great efforts have been made to design, synthesize and investigate organic molecules with TPA to meet actual requirements. Up to now, several strategies have been employed to increase the two-photon activities of organic molecules. Generally, there are three essential components that are required for two-photon chromophores, namely a π-electron donor (D), a polarizable π-bridge (π) and a π-electron acceptor (A). Appropriate combinations and numbers of these components can result in tailor-made molecules that are typically grouped into the following classes: dipole,[7] quadrupole,[8] dendrimer,[9] octupolar molecules[10] and multibranched molecules.[11] In terms of the dipole molecules, D-π-A is a typical representative; a large number of D-π-A molecules with TPA have been developed in recent years, and their structure and properties have been investigated theoretically or experimentally in detail.[12] However, to date, there has been relatively little research on D-π-D′-type molecules, which is also one of the useful molecular models to achieve desired TPA materials.[13] As is well known, many organic groups with electron-donating capacity are available, as opposed to electron-accepting ones,[7–12] which would provide an easier way to fabricate more species of TPA materials.

Recently, two D-π-D′ model chromophores with two weak electronic donors of carbazole and a sulfur-containing group were successfully prepared to give efficient blue single- and two-photon emission.[14] Here, we present continuing work, where the amine group, with a stronger electron donating ability, is introduced into a sulfur-containing styryl bridge to construct novel D-π-D′ molecules, and substituents on the sulfur atom are changed to investigate the influence on their optical properties, such as emission or excitation wavelengths, TPA responses and

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so on. Consequently, three novel D-π-D′ type chromophores with *tert*-butyl, benzyl and hydrogen on the sulfur atom were prepared. All three chromophores were fully characterized, and structure–property relationships were established. The experimental results confirm that the novel chromophores obtained are provided with single- and two-photon activities. Efficient blue-green emissions are obtained with tunable short-pulse lasers; meanwhile, Stokes' shifts and solvatochromism similar to those of asymmetrical dipole D-π-A molecules are observed. Dual emission in less polar solvents and single strongly solvent-polarity-dependent emission in more polar solvents are present. The phenomena are frequently reported for conjugated donor–acceptor (D-A) or D-π-A compounds[15] and are easily interpreted by the widely accepted twisted internal charge transfer (TICT) model suggested by Grabowski and coworkers.[16] Furthermore, it was found that different substituents on the sulfur atom had an influence on the optical properties of the related molecules. It is notable that the maximum TPA across-sections of the new model of the chromophores are clearly located in the range 700–800 nm, which is easily available from laser sources, compared with those of previous dyes we reported.[14]

Results and Discussion

Linear Absorption and Single-photon Excited Fluorescence Spectra

The photophysical properties of the three chromophores are summarized in Table 1. The linear absorption spectra of the three chromophores were measured in solvents of different polarity at a concentration of $1 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$. From the spectra (Fig. 1), peaks at ~360 nm can be readily observed for **S1** and **S2**, and at 340 nm for **S3**. The absorptions are ascribed to the π–π* transition of the π-conjugated molecular system. Absorption profiles and maximum wavelengths are very similar for **S1**–**2**, and **S3** shows the lowest maximum wavelength. Because the three molecules all have same amine terminal group, the similarities or differences in their absorption spectra must arise from the terminal groups containing sulfur. It can be interpreted in the way that the alkyl substituents (in **S1**–**2**) affect the distribution of electronic clouds on the sulfur atom, weakening the electron-donating capacity of the sulfur atom; however, the hydrogen (in **S3**) does little to this distribution. As shown in Figs A1, A2 (Accessory Publication) and Table 1, the linear absorption spectra of the three chromophores show almost no solvatochromism, indicating that surrounding solvent molecules have little influence on the π–π* transition energy of the molecules.

The single-photon excited fluorescence (SPEF) spectra were measured at the same concentration as that of the linear absorption spectra. The SPEF spectra in different solvents were also measured (Figs 2 and A2), and the wavelength maxima are clearly located in the blue-green spectral range. From Fig. 1, one can see that under the same measurement conditions, SPEF spectra showed a similar trend to linear adsorption: the spectra

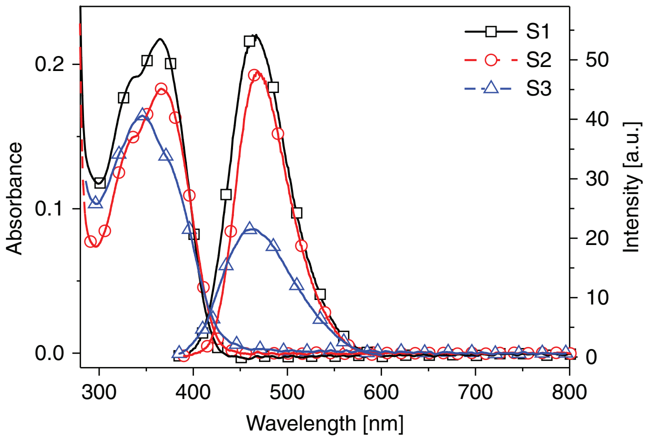


Fig. 1. Linear absorption and SPEF (single-photon excited fluorescence) spectra of **S1**–**3** in DMF.

Table 1. Photophysical properties of S1–3

Compounds	Solvent	λ^{A} [nm]	ε^{B} ($\times 10^{4}$)	λ^{C} [nm]	τ^{D} [ns]	Φ^{E}	λ^{F} [nm]
S1	DMF	364	2.18	467	0.06	0.07	–
	Ethanol	360	2.34	452	–	0.05	–
	THF	360	2.57	448	–	0.08	–
	Toluene	364	2.31	426, 439	0.31	0.12	444, 483
	Cyclohexane	360	2.27	401, 423	–	0.15	–
S2	DMF	366	1.83	468	0.06	0.08	–
	Ethanol	362	1.98	451	–	0.06	–
	THF	336	2.09	448	–	0.07	–
	Toluene	366	1.96	430, 443	0.32	0.08	445, 484
	Cyclohexane	364	2.04	400, 424	–	0.10	–
S3	DMF	345	1.64	461	0.29	0.06	–
	Ethanol	338	1.76	453	–	0.02	–
	THF	335	1.91	465	–	0.07	–
	Toluene	340	1.56	423	1.58	0.04	470
	Cyclohexane	340	1.60	403, 424	–	0.05	–

[A] λ_{max} of the one-photon absorption spectra.
[B] Corresponding molar absorption coefficient.
[C] λ_{max} of the SPEF (single-photon excited fluorescence) spectra.
[D] Lifetime of SPEF (single-photon excited fluorescence).
[E] Fluorescence quantum yield.
[F] λ_{max} of the TPEF (two-photon excited fluorescence) spectra.

of **S1**–**2** have slight red shifts relative to that of **S3**, and **S1** shows the most efficient emission. As shown in Figs 2 and A2, it is obvious that there is solvatochromism for **S1**–**3** in cyclohexane and other solvents. This hints that the first excited state of the three chromophores possesses larger dipole moments, causing strong dipole–dipole interactions between the solute and solvent, as solvatochromism is due to the energy lowering of the excited state.[17] The change of solvent polarity influences not only the energy of the emission transition but also the fluorescence quantum yields as well as the fluorescence lifetimes (Table 1). The highest fluorescence quantum yield was observed in non-polar solvents and the lowest in polar solvents. The dependence of the fluorescence lifetime on solvent polarity corresponds to the fluorescence quantum yield. The longest fluorescence lifetimes were observed in toluene, whereas the shortest was found in DMF.

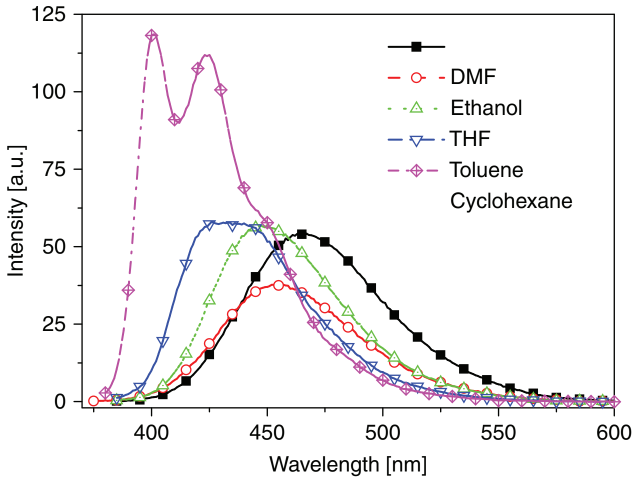


Fig. 2. SPEF (single-photon excited fluorescence) spectra of **S1** in different solvents.

As shown in Figs 2 and A2, it is notable that the obtained chromophores show dual emissions in less polar solvents, and single strongly solvent-polarity-dependent emissions in more polar solvents. According to the TICT model,[16] after excitation into a locally excited state, the dialkylamino group rotates from the planar conformation into a lower-energy perpendicular conformation, and the structure isomerizes into a TICT state (as shown in Fig. 3). The TICT state possesses a larger dipole moment compared with the ground state, so it is more stable in more polar solvents. However, because the TICT state may rapidly non-radiatively transit to a triplet state, it results in a marked decrease in the fluorescence quantum yield with a rise in solvent polarity. Clearly, the emissions of the chromophores with D-π-D′ structure in this work agree with the TICT model, similarly to the reported D-π-A chromophores.[18] As shown in Scheme 1, chromophores **S1**–**3** contain both amine and sulfur electron-donors in a single molecule, but the sulfur group is a weaker electron donor than the amine, so the D-π-D′ type chromophores **S1**–**3** show some characteristics of D-π-A molecules and possess stronger solvatochromism and larger dipole moments in comparison with those of the D-π-D′ model we reported earlier.[14] The preliminary calculations shown later in this work for the planar and twisted conformations of the three novel chromophores also show that they possess dipole moments for excited states.

Two-photon Excited Fluorescence Spectra and Absorption

As shown in Fig. 1, there is no linear absorption in the range 600–800 nm for **S1**–**3**. Therefore, on excitation from 600 to 800 nm, it is impossible to produce single-photon excited fluorescence. The insert in Fig. 4 shows that the relationship between the logarithms of the two-photon excited fluorescence (TPEF) intensity (I_{out}) of **S1** and the input laser intensity (I_{in}) is an exponential line with a slope of 2.04, which gives experimental evidence of a two-photon excitation mechanism. In order to determine the wavelength position of maximum two-photon absorption and the highest up-conversion efficiency, the TPEF

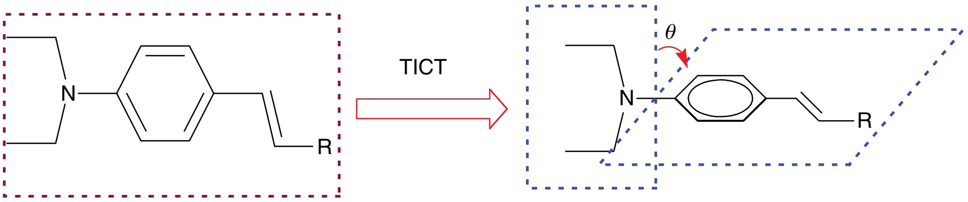
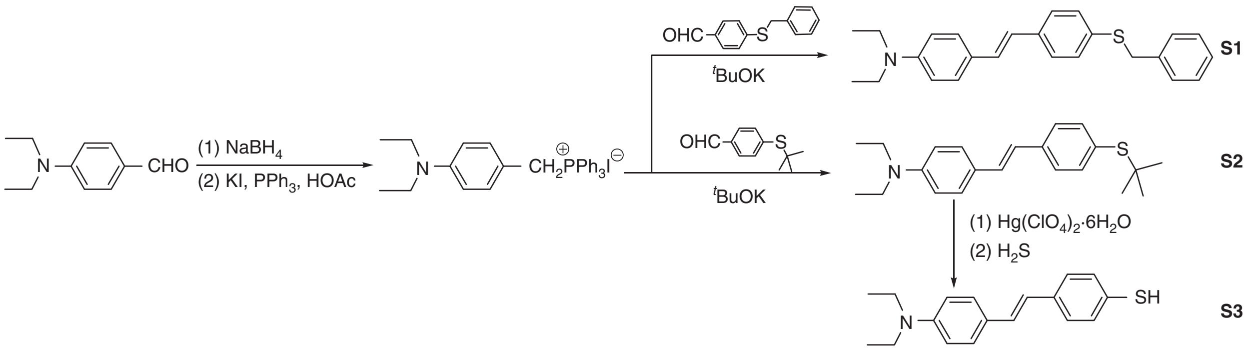


Fig. 3. Schematic illustration of twisted internal charge transfer (TICT) state.



Scheme 1. The synthesis of chromophores **S1**–**3**.

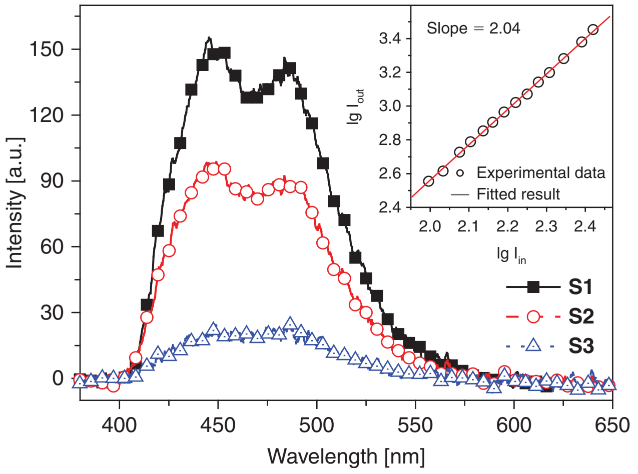


Fig. 4. The TPEF (two-photon excited fluorescence) spectra of **S1**–**3** in toluene excited at 730 nm; the insert shows the linear dependence of lg I_{out} of **S1** on lg I_{in} (I_{out}: two-photon excited fluorescence intensity; I_{in}: the input laser intensity).

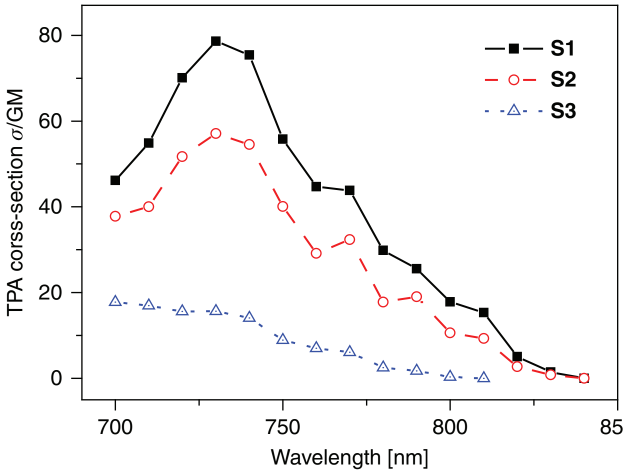


Fig. 5. TPA (two-photon absorption) cross-sections (σ, 1 GM = 10^{-50} cm^4 s photon^{-1} molecule^{-1}) for **S1**–**3** in toluene.

spectra (1.0×10^{-3} mol L^{-1} in toluene) were measured on excitation from 700 to 850 nm and with an intensity of 100 mW. Blue-green up-conversion fluorescence can be observed (Fig. 4). One finds that there are similar vibronic structures in the TPEF and SPEF spectra of the three chromophores. Some red shifts of the peak positions of TPEF spectra relative to their corresponding SPEF spectra are attributed to re-absorption from the fluorescence in the concentrated solution (Table 1). In addition to the similarities between SPEF and TPEF, the TPEF peak positions are also independent of the laser wavelength used. Thus, although the electrons can be pumped to the different excited states by linear absorption or two-photon absorption (TPA) owing to different selection rules, they would finally relax to the same lowest excited state via internal conversion and/or vibration relaxation. The dual emission was also observed for TPEF spectra in toluene, caused by a TICT process similar to that in SPEF.

The TPA cross-sections were measured using the two-photon-induced fluorescence measurement technique with the following equation:[19]

$$\sigma = \sigma_{ref} \frac{\Phi_{ref}}{\Phi} \frac{c_{ref}}{c} \frac{n_{ref}}{n} \frac{F}{F_{ref}} \tag{1}$$

Here, the subscript *ref* stands for the reference molecule; σ is the TPA cross-section value; c is the concentration of the solution; n is the refractive index of the solution; F is the integrated area of the detected two-photon-induced fluorescence signal, and Φ is the fluorescence quantum yield. The σ_{ref} values for fluorescein in H_2O (pH ~13) were taken from reference for comparison.[20] It should be noted that both the largest single-photon oscillator strength and the maximum TPA cross-section take place on the same excited state, the charge-transfer (CT) state, in the lower-energy region owing to the asymmetrical characteristics of the present molecules. Fig. 5 shows the TPA spectra of molecules **S1**–**2** with maximum absorption from 700 to 850 nm. This is because a stronger amine donor causes an obvious red shift in the maximum TPA compared with a carbazol donor in the previously reported molecules.[14] Owing to the limitations of our detecting equipment, the TPA peak values of **S3** could not be observed, but it can be expected that larger TPA cross-section values will occur below 700 nm.

Theoretical Calculation of Charge-transfer State

The experimental results above proved that the chromophores **S1**–**2** have similar single- and two-photon absorption properties, a little different from those of **S3**. To obtain more details about structure and properties relationships, theoretical calculations of the CT state were also carried out for **S1**–**3**. We used the *GAUSSIAN98* program package to optimize the molecular geometrical structure with the hybrid density functional theory (DFT/B3 LYP) and a basis set 6-31G. Our *ab initio* calculations using time-dependent hybrid density functional theory for the **S1**–**3** molecules showed that the first excited state was the CT state with the excited energy corresponding to ~350 nm. For a better understanding of the CT process, the charge density differences between the ground and CT states in the gas phase were plotted for the three molecules (as shown in Fig. 6), visualized with the *MOLEKEL* program.[21] From Fig. 6, it can be seen that the substituents on the sulfur atom in **S1**–**3** have taken part in the CT process and affect the electron distribution on the sulfur atom, agreeing with the experimental observations that the substituents on the sulfur atom have an influence on the single- or two-photon absorption of the three chromophores. As shown in Fig. 6, the sulfur atom in **S3** shows a certain 'electron-donating' capacity, which is different from that in **S1** and **S2**, and also leads to a smaller dipole moment of the excited state. Furthermore, it demonstrates that charge densities are delocalized in the full single molecule, which is attributed to the high planarity of **S1**–**3**.

Conclusions

Three novel unsymmetrical D-π-D′ chromophores containing a sulfur substituent donor were obtained via the solvent-free Wittig–Horner reaction. Structure–property relationships were established. The theoretical and experimental investigations revealed that the three chromophores obtained present good single- and two-photon activities. Furthermore, it was found that dual emissions in less polar solvent, Stokes' shifts and solvatochromism, which are similar to those of asymmetrical dipole D-π-A molecules, and the linear absorption spectra were less

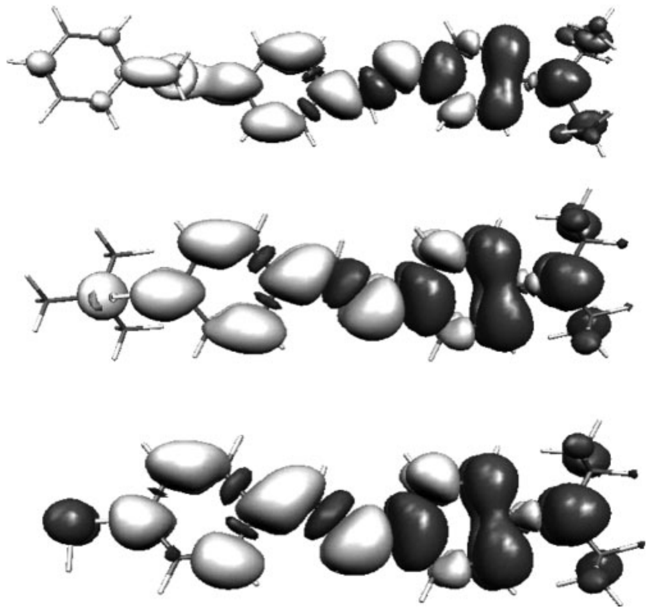


Fig. 6. Density difference between the charge-transfer and ground states of **S1**–**3** in the gas phase; grey and black areas represent the electron loss and gain, respectively, on excitation.

sensitive to the solvent polarity than the corresponding fluorescence spectra, which showed pronounced solvatochromic effects. It can be concluded that different substituents on the sulfur atom have an influence on the properties of the molecule in the appointed framework, and D-π-D′ molecules can possess a certain dipole moments similarly to D-π-A. The donor with different electron-donating capacities can be employed to tune the range of maximum TPA of D-π-D′ molecules. Therefore, the D-π-D′-type molecules should be a supplement to D-π-A- and D-π-D-type molecules to enrich the range of simple and practical TPA materials.

Experimental

Chemicals

All chemicals were available commercially and every solvent was purified by conventional methods before use. *tert*-Butylthiol, benzylthiol and 4-fluorobenzaldehyde were purchased from Aldrich. NaOH, KI, FeS, $NaBH_4$, HOAc, $Hg(ClO_4)_2\cdot 6H_2O$, ^{t}BuOK, triphenylphosphine and diethylamide were purchased from Shanghai Reagents.

Instruments

The NMR spectra, recorded at 25°C using a Bruker Avance spectrometer, are reported in ppm relavtive to TMS (δ). Coupling constants J are given in Hertz. Mass spectra were determined with a Micromass GCT-MS (EI (electron ionization) source). Electrospray ionization mass spectra (ESI-MS) were acquired with a model LCQ ion-trap mass spectrometer (Finnigan) equipped with a Finnigan MAT electrospray ion source. IR spectra were recorded on a NEXUS 870 (Nicolet) spectrophotometer in the 400–4000 cm^{-1} region using a powder sample in a KBr plate.

UV-vis absorption spectra were recorded on a UV-3100 spectrophotometer. Fluorescence measurements were carried out with an Edinburgh FLS920 fluorescence spectrometer equipped with a 450-W Xe lamp and a time-correlated single-photon counting (TCSPC) card. All the fluorescence spectra were collected. The SPEF quantum yields were measured using a standard method under the same experimental conditions for all compounds. Coumarin 307 dissolved in ethanol ($\Phi = 0.56$),[22] at the same concentration as the other samples, was used as the standard. Lifetime values were obtained by reconvolution fit analysis of the decay profiles with the aid of *F900* analysis software. The fitting results were judged by their values of 'reduced chi-squared'. TPEF spectra were measured using a mode-locked Ti:sappire femtosecond laser (Spectra-Physics, Tsunami 3941, 700–910 nm, 80 MHz, <120 fs), which was pumped by a compact CW ProLite diode laser (Spectra-Physics, Millennia Pro 5S). The fluorescence signal was recorded with a fluorescence spectrophotometer (Ocean Optics, USB2000). All measurements were carried out in air at room temperature. TPA cross-sections were measured using the two-photon-induced fluorescence measurement technique.

Synthesis and Characterization

The synthetic routes for the three chromophores **S1**, **S2** and **S3** are outlined in Scheme 1. 4-(*N*,*N*-diethylamino)benzaldehyde, (4-(diethylamino)benzyl)triphenylphosphinium iodide,[23] 4-(benzylthio)benzaldehyde and 4-(*tert*-butylthio)benzaldehyde[24] were synthesized according to references. It is important to note that the *tert*-butyl group on the sulfur atom in **S2** could be easily replaced by a hydrogen atom in the given deprotection reaction, leading to compound **S3**, and the solvent-free Wittig reaction was used to produce the *trans* isomer.[25]

(E)-4-(4-(Benzylthio)styryl)-N,N-diethylbenzenamine ***S1***

t-BuOK (3.36 g, 30 mmol) was placed in a dry mortar and milled to very tiny particles, then (4-(diethylamino)benzyl) triphenylphosphinium iodide (5.51 g, 10 mmol) and 4-(benzylthio)benzaldehyde (2.28 g, 10 mmol) were added and mixed. The mixture was milled vigorously for ~15 min, and became sticky. Anhydrous Na_2SO_4 (1 g) was added, and then the mixture was continuously milled for additional 10 min. After completion of the reaction (monitored by TLC), the mixture was dispersed in water (100 mL). The solution was extracted with CH_2Cl_2 three times. The organic layer was washed with water, then saturated brine, and dried over anhydrous magnesium sulfate. The solvent was removed under vacuum; the residue was purified by silica gel chromatography,with petroleum/ethyl acetate (50:1) as eluent. The strongly green fluorescent product was collected to give product **S1** (2.61 g, yield 70%). *m*/*z* 373.17, 268.12 (100%). *m*/*z* (ESI) $[M+1]^+$ 374.2. δ_H ([D6]DMSO, 400 MHz) 7.43 (d, 2H, J 8.27), 7.40–7.33 (m, 4H), 7.33–7.26 (m, 4H), 7.26–7.20 (m, 1H), 7.07 (d, 1H, J 16.39), 6.87 (d, 1H, J 16.37), 6.65 (d, 2H, J 8.66), 4.23 (s, 2H), 3.36 (dd, 4H, J 7.38, 7.37), 1.10 (t, 6H, J 6.97).

(E)-4-(4-(tert-Butylthio)styryl)-N,N-diethylbenzenamine ***S2***

This was prepared similarly to **S1** via (4-(diethylamino) benzyl)triphenylphosphinium iodide and 4-(*tert*-butylthio) benzaldehyde to afford the solid product **S2** (2.21 g, yield 65%). *m*/*z* 339.20, 268.11 (100%). δ_H ([D6]DMSO, 500 MHz) 7.42 (d, 2H, J 8.68), 7.52 (d, 2H, J 8.06), 7.24 (d, 2H, J 8.11), 7.16 (d, 1H, J 16.32), 6.82 (d, 1H, J 16.33), 6.66 (d, 2H, J 8.61), 3.36 (m, 4H), 1.24 (s, 9H), 1.10 (t, 6H, J 6.95).

(E)-4-(4-(Thio)styryl)-N,N-diethylbenzenamine ***S3***

S2 (2.04 g, 6 mmol) was dissolved in CH_2Cl_2 (25 mL). A 12-mmol portion of $Hg(ClO_4)_2 \cdot 6H_2O$ in methanol (10 mL) was added under stirring. A yellow precipitate appeared immediately. The reaction mixture was stirred for additional 30 min; thereafter, freshly prepared H_2S was bubbled into the solution and a black precipitate of HgS appeared. The mixture was filtered and the solid was washed with CH_2Cl_2. The organic solution was washed with water (2×50 mL), 5% $NaHCO_3$ (50 mL), and water (50 mL) and dried over anhydrous magnesium sulfate. The solvent was removed at 40°C under vacuum and the product was crystallized from hexane/2-propanol to give **S3** (1.03 g, yield 61%). *m*/*z* 284.14, 268.12 (100%). *m*/*z* (ESI) $[M+1]^+$ 340.20. ν_{max} (KBr)/cm^{-1} 2550 ($\nu_{S\text{–}H}$). δ_H ([D6] DMSO, 500 MHz) 7.39 (d, 2H, *J* 8.18), 7.36 (d, 2H, *J* 8.66), 7.24 (d, 2H, *J* 8.11), 7.04 (d, 1H, *J* 16.36), 6.85 (d, 1H, *J* 16.36), 6.65 (d, 2H, *J* 8.33), 3.35 (m, 4H), 1.09 (t, 6H, *J* 6.92).

Accessory Publication

Supporting information can be found in the web version of this paper.

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