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Benzothiazoles with Tunable Electron-Withdrawing Strength and Reverse Polarity: A Route to Triphenylamine-Based Chromophores with Enhanced Two-Photon Absorption

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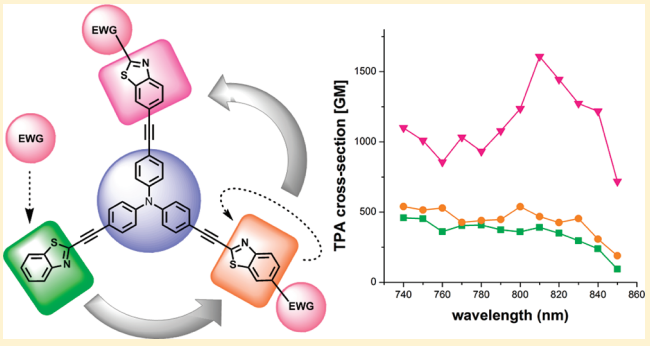
Supporting Information

ABSTRACT: A series of dipolar and octupolar triphenylamine-derived dyes containing a benzothiazole positioned in the matched or mismatched fashion have been designed and synthesized via palladium-catalyzed Sonogashira cross-coupling reactions. Linear and nonlinear optical properties of the designed molecules were tuned by an additional electron-withdrawing group (EWG) and by changing the relative positions of the donor and acceptor substituents on the heterocyclic ring. This allowed us to examine the effect of positional isomerism and extend the structure−property relationships useful in the engineering of novel heteroaromatic-based systems with enhanced two-photon absorption (TPA). The TPA cross-sections (δ_{TPA}) in the target compounds dramatically increased with the branching of the triphenylamine core and with the strength of the auxiliary acceptor. In addition, a change from the commonly used polarity in push−pull benzothiazoles to a reverse one has been revealed as a particularly useful strategy (regioisomeric control) for enhancing TPA cross-sections and shifting the absorption and emission maxima to longer wavelengths. The maximum TPA cross-sections of the star-shaped three-branched triphenylamines are ~500−2300 GM in the near-infrared region (740−810 nm); thereby the molecular weight normalized δ_{TPA}/MW values of the best performing dyes within the series (2.0−2.4 GM·g^{-1}·mol) are comparable to those of the most efficient TPA chromophores reported to date. The large TPA cross-sections combined with high emission quantum yields and large Stokes shifts make these compounds excellent candidates for various TPA applications, including two-photon fluorescence microscopy.



INTRODUCTION

Materials exhibiting large two-photon absorption (TPA)[1] are currently of great interest because of their applications in various fields such as multiphoton fluorescence microscopy,[2] three-dimensional (3D) optical data storage,[3] optical power limiting,[4] photodynamic cancer therapy,[5] and microfabrication.[6] Particularly, the two-photon excitation fluorescence (TPEF) microscopy evolved into a powerful and widely used tool in bioimaging, given the ability to capitalize on its advantages over conventional one-photon microscopy. Such advantages are intrinsic 3D resolution combined with reduced cell damage, increased in-depth tissue penetration, and negligible background fluorescence. However, most of the commonly used commercial dyes and fluorescent probes have small TPA cross-sections (δ_{TPA}), and high laser pulse energies are required to increase the probability of two-photon absorption. Therefore, to fully exploit the great potential of the TPA process, search for new compounds exhibiting large δ_{TPA} values is still one of the hot topics in the field of functional materials. In recent years, a variety of dipolar (donor−bridge−acceptor, D−π−A), quadrupolar (D-π-D, D-π-A-π-D, A-π-D-π-A), and multibranched molecules have been synthesized, and their structure−property relationships were investigated.[1,7] These studies revealed that the TPA cross-section increases mainly with the conjugation length, planarity and dimensionality of the π-center, the vibronic coupling, and the donor/acceptor strength. Apart from the high δ_{TPA} values, TPA chromophores have to satisfy various requirements, depending on the specific application. For instance, a large TPA cross-section combined with a high fluorescence quantum yield

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in the long-wavelength range (near the ideal imaging window 650−900 nm) is required for biological imaging, whereas a strong fluorescence is undesirable for two-photon-induced polymerization (TPIP). Further design criteria include excellent photostability, proper water solubility, and good cell permeability, whereby the latter property is dependent upon the molecular weight and thus limited by the size of the molecule. In this context, a convenient strategy for achieving the desired properties is to optimize the individual fragments and their position in the resulting chromophores to get the best TPA activity as possible in a small molecular space.

From a literature survey, a benzothiazole unit is an attractive building block for the construction of dyes with enhanced two-photon absorption,[8−10] or nonlinear optical (NLO) response in general,[11−14] because of its electron-withdrawing character as well as its high chemical and photophysical stability compared to the other heteroaromatics. This heterocyclic scaffold is often employed as an edge substituent, but its successful use as the π-center in quasi-quadrupolar systems with a general setup D-π-A-π-D has been also reported very recently.[8] The electron-withdrawing strength of the benzothiazole itself is, however, not sufficient to achieve very large TPA cross-sections, but it can be easily adjusted by the quaternization of the azole nitrogen or introduction of an additional acceptor. Besides, due to the unsymmetrical nature of the benzothiazole, there are several possibilities of how to arrange electron-donating (EDG) and electron-withdrawing (EWG) groups on it. It has been shown that the most efficient charge-transfer between these two functionalities is achieved when they are attached to the C-2 and C-6 positions of the benzothiazole.[11,13] Furthermore, as the strength of an additional acceptor is increased, the increase in the NLO response becomes more sensitive to its position. In general, the stronger the acceptor introduced to the benzothiazole, the more important the placement of this group at the C-2 position to obtain larger NLO response. This behavior can be simply rationalized by a concept of matched/mismatched arrangement of the 1,3-benzothiazole unit with respect to electron-donating and electron-withdrawing substituents (Figure 1).[13,15]

In the matched case, a virtual dipole between the more electron-rich benzene ring of the benzothiazole and the electron-poor C-2 position is oriented in the same direction as the intramolecular charge-transfer (ICT) and thus reinforces the excited-state dipole moment (cf., Figure 1). This results in a larger change of the dipole moment between the ground and the first excited state. Moreover, the matched alignment of the EWG leads to a better stabilization of the lowest unoccupied molecular orbital (LUMO) and thus to smaller excitation energy with the increase of the EWG strength. Both these factors are essential prerequisites for larger NLO response of the matched-type series. The same "umpolung" strategy can be also extended to TPA phenomena, as proved by our calculations on a series of dipolar benzothiazole-containing molecules using the quadratic response time-dependent density functional theory (DFT) method[16−18] (cf., Tables S1 and S2 in Supporting Information for results obtained by using the Coulomb-attenuated CAM-B3LYP functional in vacuo and in solution, respectively). Similar effects of the positional isomerism on TPA properties have been also theoretically predicted very recently in a family of triazole- and thiazole-based chromophores, respectively.[19] Although the DFT method often provides an improper description of the excited states with pronounced charge-transfer character, this problem is overcome to some extent by the use of long-range

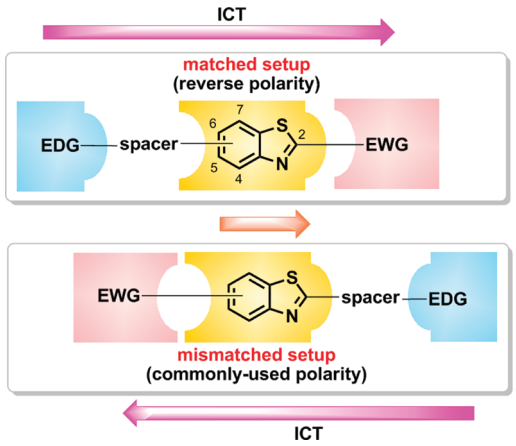

Figure 1. Schematic structure of push−pull chromophores with matched and mismatched alignment of the benzothiazole with respect to electron-donating (EDG) and electron-withdrawing (EWG) groups.

corrected functionals such as CAM-B3LYP.[20] The reliability of this method for predicting the correct structure−property relations for TPA cross-sections of organic chromophores has been shown in previous systematic studies.[8,17]

Aware of these findings, we were astonished that most of the benzothiazole-derived NLO-phores or TPA dyes known to date are designed in the mismatched alignment ("commonly-used polarity"). Only a few compounds showing the matched setup ("reverse polarity") with the confined conjugation length or without an additional EWG were prepared very recently.[21] However, because of the absence of the corresponding mismatched-type congeners or an auxiliary acceptor, these systems did not allow to examine the effect of positional isomerism on NLO properties.

To verify the trends predicted by quantum-chemical calculations, we present herein the synthesis and photophysical properties of a series of dipolar **D1**−**D6** and three-branched (octupolar, C_3-symmetric) **T1**−**T6** chromophores containing a benzothiazole moiety positioned in the matched or mismatched fashion (Scheme 1). An additional substituent R introduced to the benzothiazole allows for the fine-tuning of the linear and nonlinear optical properties at the same time. In view of the good performance of the triphenylamine framework in TPA dyes,[22] this moiety, acting as a strong electron donor and efficient π-electron bridge, was employed in each structure, either as the core or the peripheral unit. Despite the fact that a double bond is a somewhat more efficient π-conjugation bridge than a triple bond, we chose to incorporate an ethynylene π-spacer into our chromophores because of the improved photostability, absence of E/Z isomerization, and generally higher fluorescence quantum yields.[8,23]

RESULTS AND DISCUSSION

1. Synthesis. The synthetic route to the target molecules takes advantage of a palladium-catalyzed Sonogashira cross-coupling reaction between (4-*N*,*N*-diphenylamino)phenylacetylene (**1**) or tris(4-ethynylphenyl)amine (**2**) and a benzothiazole with a halogen atom (Br or I, respectively) in the C-2 or C-6 position (**3a**,**b** and **4a**,**b**, respectively) (Scheme 1). The dicyanovinyl (DCV)-substituted derivatives were prepared from the corresponding carbaldehydes by a base-catalyzed Knoevenagel condensation with malononitrile.

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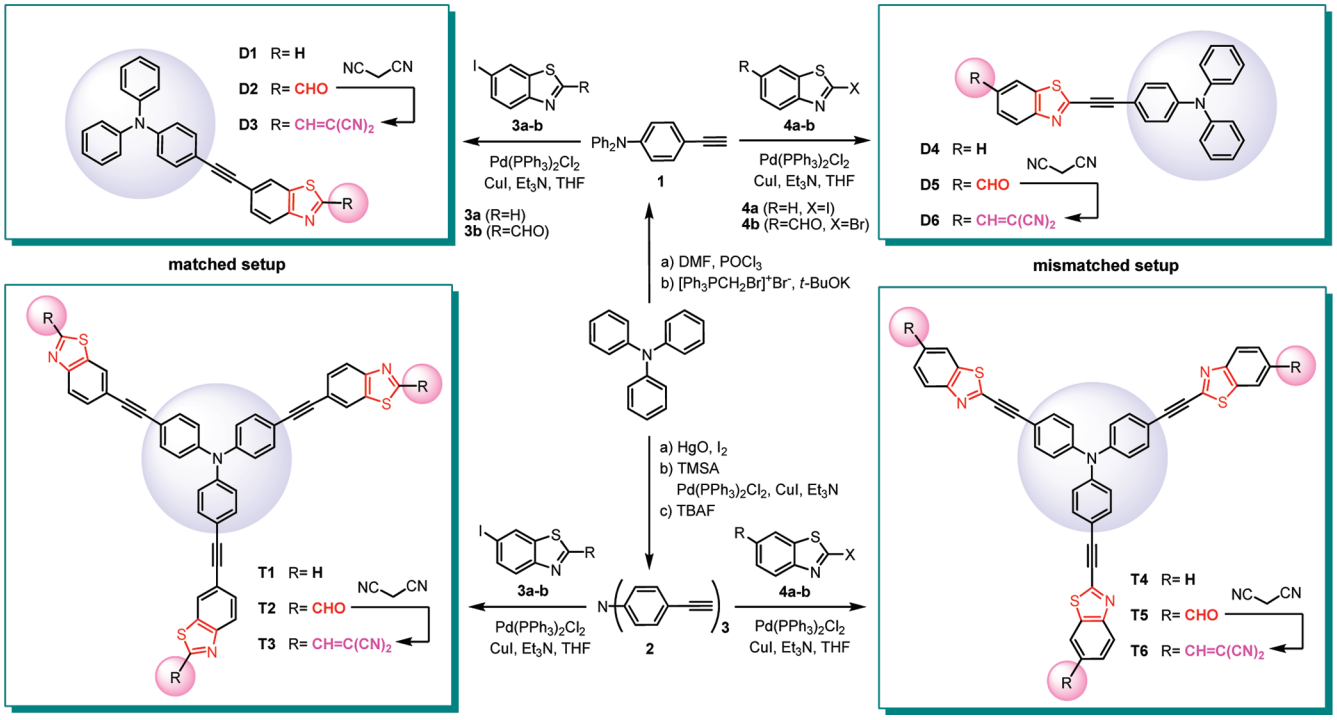
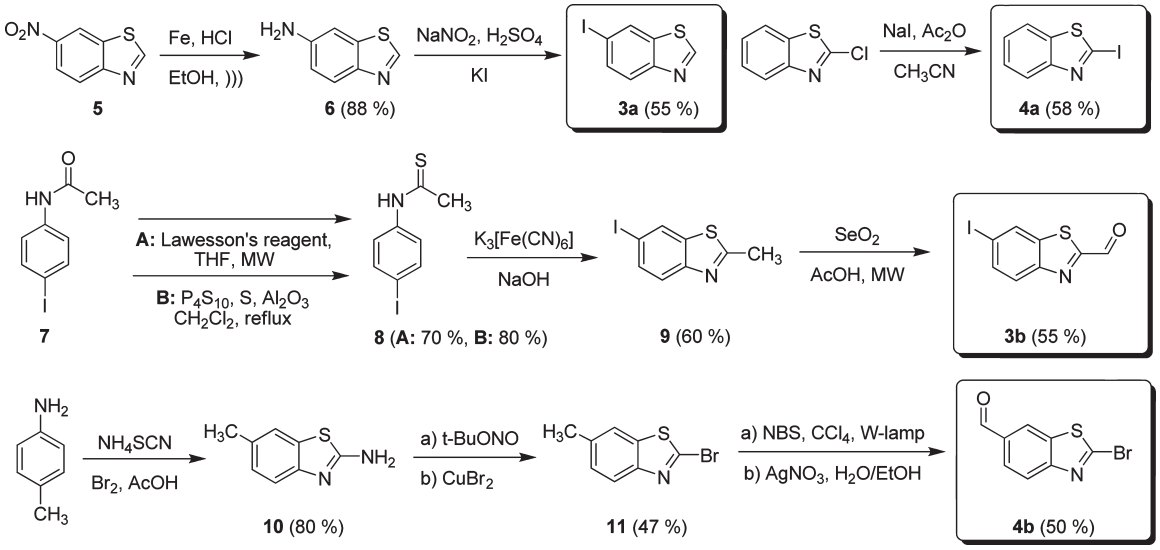
Scheme 1. Structure and Synthesis of the Target Chromophores D1−D6 and T1−T6



Scheme 2. Synthesis of the Halogen-Substituted Benzothiazoles 3a,b and 4a,b



The starting phenylacetylene **1** was obtained from the 4-(*N*,*N*-diphenylamino)benzaldehyde by using a Wittig-type condensation with (bromomethyl)triphenylphosphonium bromide in the presence of excess potassium *tert*-butoxide.[8] Tris(4-ethynylphenyl)amine (**2**) was prepared in high yield via triple Sonogashira-type reaction of tris(4-iodophenyl)amine with trimethylsilylacetylene (TMSA) and subsequent deprotection of the TMS moiety with tetrabutylammonium fluoride (TBAF)[24] (Scheme 1).

6-Iodobenzothiazole (**3a**) was prepared by the nitration of benzothiazole, subsequent sonochemical reduction of 6-nitrobenzothiazole (**5**) to amine **6**, and replacement of the NH_2 group with iodine via diazonium salt (Scheme 2). 2-Iodobenzothiazole (**4a**) was obtained in good yield (58%) from the commercially available 2-chlorobenzothiazole by nucleophilic substitution of chlorine by iodine in the presence of acetyl chloride.

The hitherto unknown 6-iodobenzothiazole-2-carbaldehyde (**3b**), which can serve as a versatile building block for the synthesis of benzothiazole-derived NLO-phores with extended π-conjugation and reverse polarity, was obtained by a sequence of reactions shown in Scheme 2: 4-Iodoaniline was almost quantitatively converted to *N*-(4-iodophenyl)acetamide (**7**) with acetic acid anhydride. The subsequent substitution of oxygen by

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Table 1. Photophysical Properties Measured in Toluene

compd	λ_{abs}[a] (nm)	E_{max}[b] (eV)	ε_{max}[c] ($M^{-1}\cdot cm^{-1}$)	λ_f[d] (nm)	Φ_f[e]	$\Delta\tilde{\nu}$[f] (cm^{-1})	λ_{TPA}[g] (nm)	δ_{TPA}[h] (GM)	δ_{TPA}/MW[i] ($GM\cdot g^{-1}\cdot mol$)
D1	365	3.40	40000	428	0.23	4033	740	<50	<0.12
D2	412	3.01	26400	519	0.57	5004	810	938	2.18
D3	494	2.51	6200	617	0.07	4035	–	–	–
							740	256	0.53
D4	388	3.20	37500	437	0.62	2890	740	<50	<0.12
	(403)[j]	(3.08)[j]	(19700)[j]	(531)[j]	(0.24)[j]	(5981)[j]	(740)[j]	(16)[j]	(0.04)[j]
D5	411	3.02	37400	473	1.00	3189	810	483	1.12
D6	457	2.71	35700	535	0.47	3190	840	821	1.72
T1	380	3.26	91000	414	0.53	2161	740	570	0.79
T2	414	3.00	46600	500	0.65	4155	810	1607	2.00
T3	480	2.58	45700	594	0.29	3998	–	–	–
							740	922	0.98
T4	404	3.07	115400	434	0.80	1711	740	459	0.64
	(433)[j]	(2.86)[j]	(89200)[j]	(538)[j]	(0.54)[j]	(4507)[j]	(740)[j]	(345)[j]	(0.48)[j]
T5	421	2.95	87500	458	1.00	1919	810	538	0.67
T6	440	2.82	54100	512	0.61	3196	800	2275	2.41

[a] Wavelength of maximum absorbance (measured at the concentration of 1×10^{-6} M at 298 K). [b] Excitation energy. [c] Molar extinction coefficient. [d] Wavelength of maximum emission. [e] Fluorescence quantum yield. [f] Stokes shift, $\Delta\tilde{\nu} = (1/\lambda_{abs} - 1/\lambda_f) \times 10^7$. [g] Wavelength of maximum TPA cross-section. [h] TPA cross-section (1 GM = 10^{-50} $cm^4\cdot s\cdot photon^{-1}$). [i] Normalized TPA cross-section (MW is the molecular weight). [j] Experimental data for analogous systems with ethenylene π-linkages instead of ethynylene ones measured in dichloromethane. Values taken from ref 9.

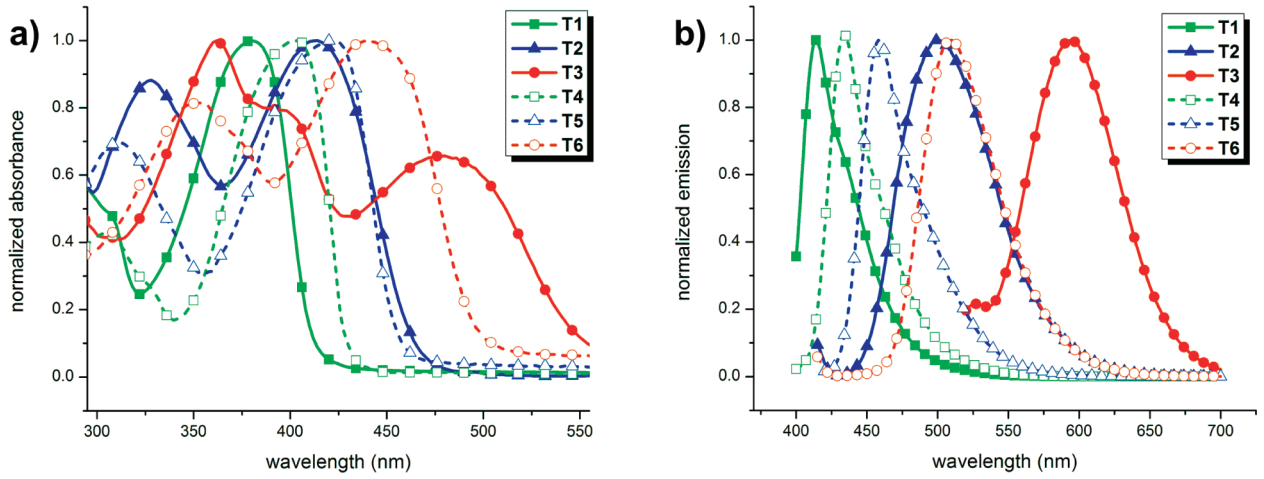

Figure 2. Normalized one-photon absorption (a) and emission (b) spectra of the three-branched chromophores **T1**−**T6** with matched (solid line) and mismatched (dashed line) setup of the benzothiazole.

sulfur, to provide the thioacetamide **8**, was examined using two different methods, either by treatment with Lawesson's reagent under microwave irradiation[25] (70% yield) or by heating under reflux with P_4S_{10} and Al_2O_3 as a solid support[26] (80% yield). The latter method has been found to be more efficient, not only due to higher yields but also because of the inexpensive reagent, simple reaction conditions, and a cleaner product. The reaction with Lawesson's reagent resulted in the formation of byproducts derived from the reagent itself, which cannot be easily removed. 6-Iodo-2-methylbenzothiazole (**9**) was prepared from **8** via Jacobson's cyclization using potassium ferricyanide in an aqueous solution of NaOH (60% yield). The synthetic route to **9** presented herein offers a somewhat improved overall yield and allows the synthesis on a larger scale compared to the procedure described in ref 8. Finally, the last step involved a microwave-assisted oxidation of the 2-methyl group of **9** with selenium dioxide. We have found that **9** was largely immune to the action of SeO_2 in common solvents such as ethanol, dioxane, or a mixture of dioxane/water under conventional heating or microwave irradiation. However, a combination of glacial acetic acid as a solvent and microwave irradiation made the oxidation by SeO_2 successful and afforded the desired product **3b** in 55% yield and a short time (20 min). This approach has been found very useful and applicable also to other 2-methyl-substituted benzothiazoles. Nevertheless, the methyl oxidation of the analogous 6-(*N*,*N*-dimethylamino)-2-methylbenzothiazole[12] by SeO_2 proceeded only in nonpolar dioxane with a somewhat lower yield (25%).

2-Bromobenzothiazole-6-carbaldehyde (**4b**), which can be viewed as a counterpart of **3b**, was synthesized as follows (cf., Scheme 2): 4-Toluidine was reacted with thiocyanogen, generated in situ from NH_4SCN and Br_2 in acetic acid, to give 2-amino-substituted benzothiazole **10** in 80% yield. This was then smoothly transformed

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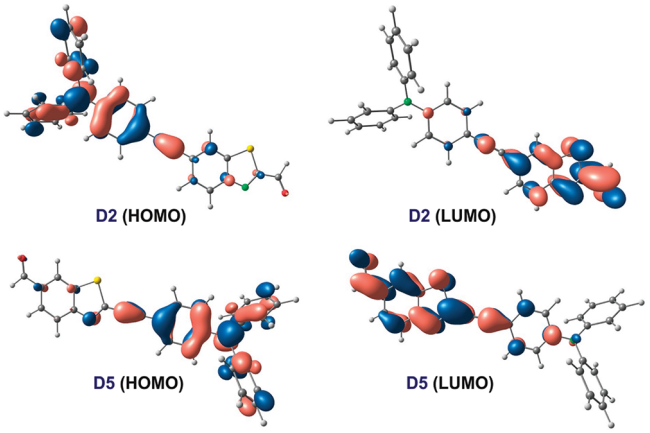

Figure 3. Frontiers orbitals of **D2** and **D5**.

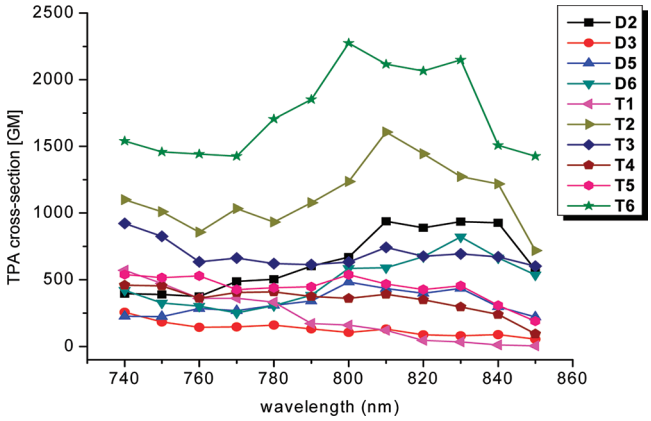

Figure 4. Two-photon absorption cross-sections δ_{TPA} (in GM units) of selected chromophores in toluene.

to 2-bromo-6-methylbenzothiazole (**11**) by means of a Sandmeyer reaction with *tert*-butyl nitrite and copper(II) bromide. In this case, we chose bromine instead of iodine because of generally higher yields of a Sandmeyer-type reaction with the former halogen and also were aware of the increased reactivity of the C-2 position in cross-coupling reactions. Microwave-assisted oxidation of **11** by SeO_2 (vide supra) afforded the expected carbaldehyde in very low yield (<10%), and therefore alternative approaches were explored. Among them, light-catalyzed bromination[27] of **11** using *N*-bromosuccinimide (NBS) and a subsequent hydrolysis of the geminal dibromo intermediate **12** was revealed as the most efficient method, providing **4b** in an overall good yield (50%).

2. One-Photon Absorption and Emission Properties. The one-photon absorption and emission characteristics of all target chromophores measured in toluene are summarized in Table 1. Corresponding UV−vis spectra of the three-branched triphenylamines, providing the first insight into the electronic structure, are shown in Figure 2a.

In general, all the compounds show an intense $\pi-\pi^*$ absorption band in the visible region, which is associated with the intramolecular-charge transfer (ICT) from the electron-donating triphenylamine moiety to the electron-withdrawing benzothiazole and adjacent EWG, if present (cf., Figure 3 for HOMO and LUMO orbitals of selected chromophores).

The maximum of this ICT band is positioned at 365 to 494 nm, depending on the substituent from the violet (R = H) to the blue-green (R = DCV) spectral region. A systematic red-shift in the λ_{abs} along the series H < CHO < CH═C$(CN)_2$ is consistent with the trend of the increasing electron-withdrawing ability and can be primarily explained by the significant stabilization of the LUMO leading to a smaller HOMO−LUMO energy gap (cf., Supporting Information, Table S3). Comparing the two regioisomeric series with matched and mismatched setup (**D1**−**D3** vs **D4**−**D6** and **T1**−**T3** vs **T4**−**T6**, respectively), it is evident that the λ_{abs} increases along the series R = H, CHO, DCV more dramatically for the compounds with reverse polarity (**D1**−**D3**, **T1**−**T3**). In the case of **D6** and **T6**, the excitation energy of the lowest energy band markedly exceeds that of the analogous DCV-substituted compounds with reverse polarity (**D3**, **T3**) by ca. 0.2 eV, that is in good agreement with our time-dependent DFT calculations (cf., Supporting Information, Table S2).

Furthermore, the three-branched compounds with R = H or CHO (**T1**, **T2**, **T4**, and **T5**) are slightly red-shifted as compared to the corresponding linear counterparts (**D1**, **D2**, **D4** and **D5**), indicating some degree of conjugation between the dipolar arms. Interestingly, octupolar systems containing the DCV group (**T3**, **T6**) behave in an opposite way and exhibit a blue-shift with respect to their dipolar congeners (**D3**, **D6**).

Comparing extinction coefficients ε_{max}, stronger absorption is generally observed for compounds with the commonly used polarity (with ε_{max} up to 115 400 $M^{-1}\cdot cm^{-1}$ for **T4**). This correlates well with their larger calculated oscillator strengths, f_{osc}, and can be qualitatively understood by inspecting the HOMO and LUMO orbitals in Figure 3. While no obvious difference between the HOMOs of the **D2** and **D5** can be noticed, in the case of LUMOs, there is a larger contribution from the atomic p_z orbitals of the triphenylamine moiety in the mismatched-type compound **D5**. This results in a better overlap of the frontier orbitals and thus larger oscillator strengths of this series.

All chromophores under study display moderate to excellent emission in toluene solution with fluorescence quantum yields ranging from 0.07 (**D3**) to 1.00 (**D5**, **T5**). The quantum yield generally increases with the dimensionality of the molecule, and it reaches higher values for the compounds with commonly used polarity. The fluorescence spectra exhibit a single peak (cf., Figure 2b), suggesting that the emission occurs from the lowest excited state. The emission maxima are spread over a wide range of wavelengths (428−617 nm), from the blue (**D1**, **D4**, **T1**, **T4**) to the orange-red spectral region (**D3**, **T3**). Similarly to absorption, the emission spectra show systematic bathochromic shifts with the EWG strength increase, that is H < CHO < CH═C$(CN)_2$.

In contrast, the fluorescence Stokes shift, $\Delta\tilde{\nu}$, displays a nonmonotonous behavior, particularly within the series of dyes with reverse polarity (**D1**−**D3**, **T1**−**T3**). Furthermore, the compounds from this series exhibit Stokes shifts larger than those observed for their counterparts with the commonly used polarity (**D4**−**D6**, **T4**−**T6**). That is presumably because the ground-state and the first excited-state structures are more similar in the compounds with mismatched setup (commonly used polarity). This would corroborate the larger change of the dipole moment $\Delta\mu_{01}$ upon photoexcitation for the reverse polarity and will be the subject of our further investigations.

3. Two-Photon Absorption Properties. Two-photon absorption cross-sections (δ_{TPA}) were measured by the two-photon-induced fluorescence technique using femtosecond (fs) laser pulses. Due to the laser availability (Ti:sapphire laser), the

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solutions were excited in the range of 740 to 850 nm. In all cases, the output intensity of two-photon excited fluorescence was linearly dependent on the square of the input laser intensity, thereby confirming the TPA process.

All compounds, except the dipolar ones without an additional EWG substituent (**D1** and **D4**), show moderate to excellent TPA cross-sections in the range of 256−2275 GM (cf., Table 1, Figure 4). Table 1 shows that the $\lambda_{TPA}/2$ values of compounds where R = H or CHO are located at nearly the same wavelengths as the one-photon absorption maxima. This is indeed in accord with the selection rules that the two-photon allowed states of the dipolar and octupolar molecules are similar to those of the one-photon allowed states. Closer inspection of the TPA spectra reveals, however, that λ_{TPA} appears slightly blue-shifted with respect to twice the λ_{abs} wavelength, and the difference is even more pronounced for DCV derivatives. This might indicate that the transitions to higher-energy excited states, allowed by vibronic coupling, are also contributing to the signal.[28]

In general, the three-branched triphenylamines display larger TPA cross-sections than their dipolar counterparts, with the highest δ_{TPA} values for **T2** (1607 GM) and **T6** (2275 GM), located at 810 and 800 nm, respectively. These values are higher than those of the most triphenylamine-derived molecules of a similar molecular weight. Furthermore, both compounds exhibit a relatively high fluorescence quantum yield (>0.60) and could be thus promising candidates for two-photon imaging.

When the structures without an additional EWG are compared, it is obvious that the δ_{TPA} value increased by approximately 1 order of magnitude as the dimensionality was increased from mono- to three-branched structures (cf., **D1** vs **T1** and **D4** vs **T4**, respectively). The TPA cross-section of the fluorophore **T1**, possessing a matched setup, is somewhat larger than that of **T4**. This already demonstrates the superiority of the matched setup (reverse polarity) in terms of TPA cross-section, although the product $\Phi_f\delta_{TPA}$ is higher for **T4**. The difference between these regioisomeric series is further increased by CHO substitution, which dramatically boosts the δ_{TPA} value of the dipolar systems by ca. 20-fold for compounds with reverse polarity (**D1** vs **D2**) and by ca. 10-fold for compounds with commonly used polarity (**D4** vs **D5**). In the case of three-branched systems, this increase is also more pronounced for compounds with the reverse polarity (ca. 3-fold, **T1** vs **T2**), while only a small TPA enhancement (ca. 1.3-fold) is observed when passing from **T4** to **T5**. Further increase of the EWG strength from CHO to DCV leads to a dramatic TPA enhancement for the compounds with commonly used polarity (cf., **D6** vs **D5** and **T6** vs **T5**). In contrast, a remarkable drop of the TPA activity can be noticed when comparing the couples with reverse polarity **D3**/**D2** and **T3**/**T2**, respectively. The striking behavior can be, however, rationalized as follows: While most of the target chromophores have their TPA maximum associated with the first excited state in or close to the measurement range (740−850 nm), the maxima of the DCV derivatives **D3** and **T3** are anticipated, on the basis of their λ_{abs}, at longer wavelengths (>900 nm), which are not covered in the scanned optical window. This unfortunately prevents us from direct comparison of their TPA cross-sections with those of their analogues **D6** and **T6**, and it would be of interest to test these dyes also at higher excitation wavelengths in future studies.

CONCLUSIONS

In summary, we demonstrated here a facile route to triphenylamine-based chromophores with enhanced two-photon absorption by introducing an auxiliary acceptor to the pendant benzothiazole side arm and by changing the relative positions of the donor and acceptor substituents on the heteroaromatic ring. A change from the commonly used polarity in push−pull benzothiazoles to a reverse one has been revealed as a particularly useful strategy (regioisomeric control) for enhancing the TPA cross-sections and shifting the absorption and emission maxima to longer wavelengths. The values δ_{TPA}/MW determined for **D2**, **T2**, and **T6** (ca. 2.0−2.4 GM·g^{-1}.mol) are comparable to those of the most efficient TPA materials reported to date and can be easily improved further by planarization of the triphenylamine core via dialkylmethylene connectors or increasing the strength of the EWG. High TPA cross-sections combined with the easy synthetic access of these structures and with their high quantum yields make these compounds worth considering for various TPA applications. Furthermore, large hyperpolarizabilities β_0 predicted for the dipolar compounds with an additional EWG substituent (cf., Supporting Information, Tables S1 and S2) make these systems attractive simultaneously for application in TPEF as well as in second harmonic generation (SHG) imaging microscopy.

EXPERIMENTAL SECTION

1. Synthetic Procedures. *Tris(4-iodophenyl)amine.* To a solution of triphenylamine (3.0 g, 12 mmol) in ethanol (150 mL) were added HgO (12.2 g, 56 mmol) and finely powdered iodine (15.3 g, 60 mmol). The reaction mixture was stirred at room temperature for 24 h, and then the solvent was removed on a rotary evaporator. The orange solid residue was mixed with hot toluene, refluxed for 10 min, and consequently hot-filtered through a short column of Al_2O_3. Then, methanol was added to the hot toluene solution until crystals were formed. The solution was left for 12 h, and the crystals were collected by filtration to give the title product in 77% yield (5.8 g). Mp 180−182 °C (lit.[29] mp 182−184 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 9.0 Hz, 6H, H_{ar}), 6.81 (d, J = 8.8 Hz, 6H, H_{ar}).

*Tris(4-ethynylphenyl)amine (**2**).* To a mixture of (4-iodophenyl)amine (0.58 g, 0.93 mmol), $Pd(PPh_3)_2Cl_2$ (98 mg, 0.14 mmol), and copper iodide (13 mg, 0.07 mmol) was added THF (8 mL) under nitrogen, and the suspension was stirred at room temperature for 20 min. Consequently, triethylamine (5 mL, freshly distilled from CaH_2) was added, and the reaction mixture was stirred for an additional 30 min at room temperature. After this time, trimethylsilylacetylene (0.53 mL, 3.72 mmol) was added dropwise via syringe, and the reaction mixture turned black within 5 min. The mixture was stirred at room temperature for 36 h, diluted with ether (10 mL), and forced through a short pad of silica. The solid part was washed with ether, the solvent from the combined organic solutions was evaporated, and the obtained crude intermediate was dissolved in CH_2Cl_2 (10 mL). The solution was cooled to 0 °C, and TBAF (2.8 mL of 1 M solution in THF, 2.8 mmol) was added via syringe. The reaction mixture was stirred at 0−5 °C for 2.5 h and consequently absorbed onto silica. The title compound was obtained by column chromatography on silica gel (eluent hexanes/$CHCl_3$ = 3:1) in 62% yield (0.18 g). R_f 0.25 (SiO_2, hexanes/$CHCl_3$ = 3:1); mp 105.5−107 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, J = 8.6 Hz, 6H, H_{ar}), 7.01 (d, J = 8.6 Hz, 6H, H_{ar}), 3.06 (s, 3H, C≡CH).

*6-Nitrobenzothiazole (**5**).* Benzothiazole (18.2 mL, 0.17 mol) was dissolved in concentrated H_2SO_4 (46 mL). The solution was cooled to 0 °C, and 100% HNO_3 (18.2 mL) was added dropwise at such a rate to keep the temperature below 5 °C throughout the addition. After the addition was completed, the reaction mixture was stirred under cooling for 15 min and then at room temperature for an additional 2 h. Subsequently, the mixture was poured into ice-cold water (400 mL). The precipitate was collected by filtration, washed with cold water until the pH was neutral, and crystallized from ethanol to give the title compound **5** as a white solid in 68% yield (20.8 g). Mp 176−177 °C

(lit.[30] mp 177 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.28 (s, 1H, H-2), 8.93 (d, J = 2.2 Hz, 1H, H-7), 8.42 (dd, J = 9.3, 2.2 Hz, 1H, H-5), 8.26 (d, J = 9.3 Hz, 1H, H-4).

*6-Aminobenzothiazole (**6**).* To a mixture of 6-nitrobenzothiazole (**5**) (4.8 g, 26.6 mmol) and concentrated HCl (3.8 mL) in 80% ethanol (150 mL) was added powdered iron (6.0 g, 107 mmol). The reaction mixture was sonicated for 40 min and then cooled down to room temperature. Precipitated iron oxides were removed by filtration through a short pad of silica gel and washed with ethanol (2 × 30 mL). The solvent was removed, and the solid residue was extracted into a heterogeneous mixture of EtOAc and 10% aq solution of Na_2CO_3. The organic layer was dried (Na_2SO_4), and the solvent was removed under vacuum. The crude product was purified by short-column chromatography on silica gel (eluent hexanes/EtOAc = 2:1) to yield **6** (3.5 g, 88%) as a white-gray solid. R_f 0.11 (SiO_2, hexanes/EtOAc = 1:1); mp 86−87 °C (lit.[12] mp 86−87 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (s, 1H, H-2), 7.89 (d, 1H, J = 8.9 Hz, H-4), 7.16 (d, 1H, J = 2.3 Hz, H-7), 6.87 (dd, 1H, J = 8.9, 2.3 Hz, H-5), 3.86 (bs, 2H, NH_2).

*6-Iodobenzothiazole (**3a**).* A mixture of concentrated H_2SO_4 (20 mL) and $NaNO_2$ (1.3 g, 18.5 mmol) was prepared at 70 °C. After cooling to 40 °C, a solution of 6-aminobenzothiazole (**6**) (2.5 g, 16.6 mmol) in acetic acid (35 mL) was added dropwise. The reaction mixture was stirred at room temperature for 30 min, and after this time the formed diazonium salt was added to the stirred solution of KI (3.32 g, 20 mmol) in water (35 mL) and heated to 70 °C. The reaction mixture was stirred at 70 °C for 30 min and then poured onto ice. The precipitate was collected by filtration, washed with water, and dissolved in $CHCl_3$ (50 mL). The organic solution was washed with 10% aq solution of $Na_2S_2O_3$ (2 × 30 mL), dried over Na_2SO_4, and the solvent was evaporated. The crude product was crystallized from cyclohexane (20 mL) or purified by column chromatography on silica gel (eluent hexanes/EtOAc = 7:1) to yield **3a** as a white solid (2.33 g, 55%). R_f 0.55 (SiO_2, hexanes/EtOAc = 4:1); mp 78−80 °C (lit.[31] mp 79−80°); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.93 (s, 1H, H-2), 8.32 (d, J = 1.1 Hz, 1H, H-7), 7.89 (d, J = 8.8 Hz, 1H, H-4), 7.81 (dd, J = 8.8, 1.1 Hz, 1H, H-5).

4-Iodoaniline. To a solution of sodium bicarbonate (4.0 g, 48 mmol) in water (350 mL) was added aniline (2.94 mL, 32 mmol). The reaction mixture was cooled in an ice water bath, and finely powdered iodine (6.1 g, 24 mmol) was added in small portions at 3-min intervals under intensive stirring (temperature was maintained at 12−15 °C). After the addition was finished, the reaction mixture was stirred at room temperature for 40 min, and the crude product was collected by filtration and crystallized from cyclohexane (20 mL) to yield 4-iodoaniline (6.4 g, 91%) as white-gray crystals. Mp 62−63 °C (lit.[32] mp 62−63 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J = 9.0 Hz, 2H, H_{ar}), 6.48 (d, J = 9.0 Hz, 2H, H_{ar}), 3.67 (bs, 2H, NH_2).

*N-(4-Iodophenyl)acetamide (**7**).* To a solution of 4-iodoaniline (7.8 g, 36 mmol) in THF (20 mL) was added acetic anhydride (72 mmol, 6.8 mL) and 3 drops of pyridine. The reaction mixture was stirred and heated spontaneously. After cooling to room temperature, the precipitate was collected by filtration, washed with ice-cold THF and dried. The title compound was obtained in 95% yield (8.9 g). Mp 182−184 °C (lit.[33] mp 180−182 °C); ^{1}H NMR (300 MHz, DMSO) δ 10.02 (s, 1H, NH), 7.62 (d, J = 8.8 Hz, 2H, H_{ar}), 7.42 (d, J = 8.8 Hz, 2H, H_{ar}), 2.03 (s, 3H, CH_3).

*N-(4-Iodophenyl)thioacetamide (**8**). Method A.* A suspension of *N*-(4-iodophenyl)acetamide (**7**) (1.0 g, 3.8 mmol) and Lawesson's reagent (1.1 g, 2.7 mmol) in THF (15 mL) was heated under microwave irradiation (105 °C) for 15 min. The reaction mixture was poured into water (200 mL), and the aqueous layer was extracted with ether (3 × 50 mL). The combined organic layers were washed with hot water (3 × 50 mL) and brine (50 mL) and dried over Na_2SO_4, and solvents were removed under vacuum. The crude product was purified by crystallization from 60% methanol (40 mL) to give the title compound in 70% yield (0.74 g).

Method B. A suspension of *N*-(4-iodophenyl)acetamide (**7**) (1.0 g, 3.8 mmol), P_4S_{10} (1.69 g, 3.8 mmol), Al_2O_3 (200 mg), and elementary sulfur (10 mg) in dichloromethane (35 mL) was refluxed under intensive stirring for 10 h. Consequently, the hot solution was poured into water (200 mL), the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with hot water (3 × 50 mL) and brine (50 mL) and then dried over Na_2SO_4, and solvents were removed under vacuum. The crude product was purified by crystallization from 60% methanol (40 mL) to give the title compound in 80% yield (0.84 g). Mp 148−149 °C (lit.[34] mp 147−149 °C); ^{1}H NMR (300 MHz, DMSO) δ 11.62 (s, 1H, NH), 7.75 (d, J = 8.8 Hz, 2H, H_{ar}), 7.65 (d, J = 8.8 Hz, 2H, H_{ar}), 2.59 (s, 3H, CH_3).

*6-Iodo-2-methylbenzothiazole (**9**).* *N*-(4-Iodophenyl)thioacetamide (**8**) (4.0 g, 14.4 mmol) was dissolved in a 30% aqueous solution of NaOH (20 mL) under vigorous stirring and cooling in an ice bath. The resulting solution was diluted with ice−water (40 mL) and then added dropwise to an aqueous solution of $K_3[Fe(CN)_6]$ (19.0 g, 58 mmol) under intensive stirring and cooling during 4 h (note: temperature of the added solution has to be maintained below 15 °C throughout the addition). After the addition was completed, the reaction mixture was stirred at room temperature for 30 min. The precipitate was collected by filtration, washed with water, and dried. The crude product was purified by column chromatography on silica gel, eluting with dichloromethane to yield 6-iodo-2-methylbenzothiazole (**9**) as a white solid (2.18 g, 55%). R_f 0.53 (SiO_2, CH_2Cl_2); mp 140−141 °C (lit.[35] mp 140−141 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, J = 1.6 Hz, 1H, H-7), 7.73 (dd, J = 8.4, 1.6 Hz, 1H, H-5), 7.67 (d, J = 8.4 Hz, 1H, H-4), 2.82 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3, 147.6, 132.6, 129.8, 124.6, 118.7, 83.7, 14.8.

*6-Iodobenzothiazole-2-carbaldehyde (**3b**).* A suspension of 6-iodo-2-methylbenzothiazole (**9**) (1.5 g, 5.45 mmol) and SeO_2 (1.8 g, 16 mmol) in glacial acetic acid (15 mL) was heated under microwave irradiation (150 °C) for 20 min, and then the hot suspension was filtered through short column of silica. The solid part absorbed on silica was washed with boiling hot water, and the filtrate was diluted with cold water until a precipitate was formed. The precipitate was collected by filtration, washed with cold water, and dried. The solid part absorbed on silica was washed with a 30% aq solution of Na_2CO_3 (100 mL) and then with hot chloroform (100 mL). The chloroform layer was separated and dried over Na_2SO_4, and the solvent was evaporated. The solid residue was combined with the precipitate and purified by column chromatography on silica gel, eluting with dichloromethane, to yield the title compound **3b** (0.87 g, 55%) as a pale yellow solid. R_f 0.52 (SiO_2, CH_2Cl_2); mp 133−134 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.16 (s, 1H, CHO), 8.39 (d, J = 1.6 Hz, 1H, H-7), 7.97 (d, J = 8.8 Hz, 1H, H-4), 7.90 (dd, J = 8.8, 1.6 Hz, 1H, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.1, 165.5, 152.8, 138.2, 136.7, 131.3, 127.0, 94.1. Anal. Calcd for C_8H_4INOS: C 33.24, H 1.39, N 4.85. Found: C 33.41, H 1.22, N 4.99.

*2-Iodobenzothiazole (**4a**).* Acetyl chloride (7.2 mL, 0.1 mol) was added dropwise to the cooled and stirred 2-chlorobenzothiazole (17 g, 0.1 mol). After the mixture was stirred for 10 min, a solution of dry NaI (30.0 g, 0.2 mol) in acetonitrile (210 mL, freshly distilled from P_2O_5) was added. After a yellow precipitate was formed, the suspension was stirred for an additional 5 min, and consequently the precipitate was collected by filtration. The precipitate was dissolved in chloroform (150 mL), and the resulting solution was washed with 15% aq solution of K_2CO_3 (100 mL) and then with a 20% aq solution of $Na_2S_2O_5$ until the organic layer became colorless. The organic layer was separated and dried over Na_2SO_4, and chloroform was evaporated. The crude product was purified by crystallization from 80% ethanol to yield the title compound **4a** (15.1 g, 58%) as a white solid. Mp 77−78 °C (lit.[36] mp 78−82 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (dd, J = 7.3, 1.5 Hz, 1H), 7.85 (dd, J = 7.3, 1.5 Hz, 1H), 7.44 (ddd, J = 7.3, 7.3, 1.5 Hz, 1H), 7.39 (ddd, J = 7.3, 7.3, 1.5 Hz, 1H).

*2-Amino-6-methylbenzothiazole (**10**).* A mixture of 4-methylaniline (5 g, 47 mmol) and NH_4SCN (17.8 g, 234 mmol) in glacial acetic acid (50 mL) was cooled and stirred. To this solution was dropwise added bromine (2.6 mL, 51 mmol) dissolved in acetic acid (5 mL) at such a rate to keep the temperature below 10 °C throughout the addition (ca. 2−3 h). Stirring at 10−15 °C was continued for an additional 3 h, and then the reaction mixture was poured into cold water and neutralized with a 25% aqueous solution of ammonia. The solid precipitate was collected by filtration and washed with water. The crude product was purified by crystallization from benzene, respectively, by column chromatography on silica gel (eluent hexanes/EtOAc = 3:1), affording **10** in 80% yield (6.13 g). R_f 0.25 (SiO_2, hexanes/EtOAc = 1:1); mp 135−137 °C (lit.[37] 135−137 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 1H, H-4), 7.40 (d, J = 1.2 Hz, 1H, H-7), 7.12 (dd, J = 8.4, 1.2 Hz, 1H, H-5), 5.26 (bs, 2H, NH_2), 2.40 (s, 3H, CH_3).

*2-Bromo-6-methylbenzothiazole (**11**).* To a suspension of copper(II) bromide (6.52 g, 29 mmol) in acetonitrile (60 mL) was added *tert*-butyl nitrite (4.30 mL, 36 mmol). The resulting mixture was stirred at 55 °C for 10 min, and then the solid 2-amino-6-methylbenzothiazole (**10**) (4 g, 24 mmol) was added in small portions. The reaction mixture was stirred at 60 °C for 1 h. After cooling to room temperature, the reaction mixture was poured into ethyl acetate (100 mL) and washed with 1 M solution of HCl and saturated brine. The organic solution was dried over Na_2SO_4, solvents were evaporated, and the crude product was purified by column chromatography on silica gel (eluent hexanes/EtOAc = 10:1) to yield **11** as a white solid (2.58 g, 47%). R_f 0.33 (SiO_2, hexanes/EtOAc = 10:1); mp 54−56 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 1H, H-4), 7.27 (d, J = 1.5 Hz, 1H, H-7), 7.12 (dd, J = 8.4, 1.5 Hz, 1H, H-5), 2.47 (s, 3H, CH_3).

*2-Bromo-6-(dibromomethyl)benzothiazole (**12**).* A suspension of 2-bromo-6-methylbenzothiazole (**11**) (1.38 g, 5.92 mmol) and *N*-bromosuccinimide (2.10 g, 11.84 mmol) in carbon tetrachloride (130 mL) was irradiated with a tungsten lamp (125 W) for 4 h. After cooling to room temperature, the solid part was filtered off and washed with CCl_4. The organic solutions were combined, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent hexanes/EtOAc = 10:1) to yield **12** as a white solid (1.58 g, 69%). R_f 0.27 (SiO_2, hexanes/EtOAc = 10:1); mp 125−126 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J = 1.8 Hz, 1H, H-7), 7.98 (d, J = 8.4 Hz, 1H, H-4), 7.70 (dd, J = 8.4, 1.8 Hz, 1H, H-5), 6.75 (s, 1H, $CHBr_2$).

*2-Bromobenzothiazole-6-carbaldehyde (**4b**).* To a refluxed suspension of 2-bromo-6-(dibromomethyl)benzothiazole (**12**) (1.0 g, 2.58 mmol) in ethanol (15 mL) was added a solution of $AgNO_3$ (4.39 g 25.8 mmol) in water (15 mL) dropwise over 20 min. After the addition was completed, the reaction mixture was stirred at reflux for an additional 1 h, cooled to room temperature, and then poured into water (150 mL). The formed precipitate was filtered off and washed with chloroform (80 mL), and the filtrate was extracted with chloroform (3 × 20 mL). Combined organic layers were dried over Na_2SO_4, and the solvent was evaporated. The crude product was purified by column chromatography on silica gel (eluent hexanes/EtOAc = 5:1) to yield **4b** as a white solid (0.43 g, 69%). R_f 0.48 (SiO_2, hexanes/EtOAc = 5:1); mp 148−150 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.13 (s, 1H, CHO) 8.37 (d, J = 1.5 Hz, 1H, H-7), 8.13 (d, J = 8.4 Hz, 1H, H-4), 8.00 (dd, J = 8.4, 1.5 Hz, 1H, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.8, 156.0, 143.6, 138.0, 133.6, 127.6, 123.4, 123.3. Anal. Calcd for C_8H_4BrNOS: C 39.69, H 1.67, N 5.79, S 13.24. Found: C 39.74, H 1.65, N 5.70.

*General Procedure for Synthesis of **D1**−**D2**, **D4**−**D5**, **T1**−**T2**, and **T4**−**T5** (Sonogashira Cross-Coupling Reaction).* To a mixture of halogen-substituted benzothiazole (**3a**, **3b**, **4a**, or **4b**, 2.0 mmol), $Pd(PPh_3)_2Cl_2$ (84 mg, 0.12 mmol), and CuI (8 mg, 0.04 mmol) was added THF (22 mL) under nitrogen, and the resulting suspension was stirred at room temperature for 20 min. Consequently, triethylamine (10 mL, freshly distilled from CaH_2) was injected into the reaction mixture, and stirring was continued for an additional 30−90 min. Afterward, corresponding acetylene **1** (0.65 g, 2.4 mmol) or **2** (0.21 g, 0.66 mmol) dissolved in THF (3−8 mL) was added dropwise (over 30 min) with intensive stirring under an atmosphere of nitrogen (note: a large amount of white precipitate appeared after the addition of acetylene **2**). After being stirred for 24−48 h at room temperature under nitrogen, the reaction mixture was diluted with THF (10−15 mL). The precipitate was filtered and washed with CH_2Cl_2 and consequently with the mixture CH_2Cl_2/MeOH (20:1). The solvent from the combined organic solutions was evaporated under vacuum, and the crude product was purified by column chromatography on silica gel.

*6-[(4-Diphenylaminophenyl)ethyn-1-yl]benzothiazole (**D1**).* Eluent $CHCl_3$/hexanes = 2:1; yield 77% (0.62 g); R_f 0.43 (SiO_2, $CHCl_3$/hexanes = 2:1); mp 150−152 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.02 (s, 1H, H-2), 8.11 (dd, J = 1.5 Hz, 0.5 Hz, 1H, H-7), 8.08 (dd, J = 8.5 Hz, 0.5 Hz, 1H, H-4), 7.64 (dd, J = 8.5, 1.5 Hz, 1H, H-5), 7.39 (d, J = 8.8 Hz, 2H, H_{ar}), 7.31−7.27 (m, 4H, H_{ar}), 7.14−7.04 (m, 6H, H_{ar}), 7.02 (d, J = 8.8 Hz, 2H, H_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 148.1, 147.1, 133.9, 132.6, 129.6, 129.4, 125.0, 124.8, 123.6, 123.4, 122.2, 121.2, 115.6, 90.7, 88.1 (the number of ^{13}C NMR peaks is reduced due to signal overlapping). Anal. Calcd for $C_{27}H_{18}N_2S$: C 80.57, H 4.51, N 6.96. Found: C 80.50, H 4.43, N 6.90.

*6-[(4-Diphenylaminophenyl)ethyn-1-yl]benzothiazole-2-carbaldehyde (**D2**).* Eluent $CHCl_3$/MeOH = 30:1; yield 64% (0.55 g); R_f 0.73 (SiO_2, $CHCl_3$/MeOH = 30: 1); mp 171−172 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.16 (s, 1H, CHO), 8.18 (d, J = 8.5 Hz, 1H, H-4), 8.13 (d, J = 1.6 Hz, 1H, H-7), 7.71 (dd, J = 8.5, 1.6 Hz, 1H, H-5), 7.39 (d, J = 8.8 Hz, 2H, H_{ar}), 7.32−7.27 (m, 4H, H_{ar}), 7.14−7.06 (m, 6H, H_{ar}), 7.02 (d, J = 8.8 Hz, 2H, H_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.2, 165.7, 152.7, 148.5, 147.0, 136.6, 132.7, 130.7, 129.5, 125.5, 125.23, 125.20, 124.3, 123.8, 121.9, 114.9, 93.0, 87.9. Anal. Calcd for $C_{28}H_{18}N_2OS$: C 78.11, H 4.21, N 6.51. Found: C 78.28, H 4.02, N 6.68.

*2-[(4-Diphenylaminophenyl)ethyn-1-yl]benzothiazole (**D4**).* Eluent $CHCl_3$/hexanes = 3:1; yield 77% (0.62 g); R_f 0.48 (SiO_2, $CHCl_3$/hexanes = 3:1); mp 199−201 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 7.9 Hz, 1H, H_{BTZ}), 7.86 (d, J = 7.9 Hz, 1H, H_{BTZ}), 7.54−7.40 (m, 4H, $2H_{BTZ}$, $2H_{ar}$), 7.34−7.28 (m, 4H, H_{ar}), 7.15−7.09 (m, 6H, H_{ar}), 7.00 (d, J = 8.7 Hz, 2H, H_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 149.4, 149.1, 146.7, 135.3, 133.3, 129.5, 126.6, 125.9, 125.6, 124.2, 123.4, 121.2, 121.1, 112.7, 97.1, 82.3. Anal. Calcd for $C_{27}H_{18}N_2S$: C 80.57, H 4.51, N 6.96. Found: C 80.66, H 4.39, N 7.09.

*2-[(4-Diphenylaminophenyl)ethyn-1-yl]benzothiazole-6-carbaldehyde (**D5**).* Eluent hexanes/EtOAc = 5:1; yield 71% (0.61 g); R_f 0.44 (SiO_2, hexanes/EtOAc = 3: 1); mp 165−167 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.12 (s, 1H, CHO), 8.4 (d, J = 1.5 Hz, 1H, H-7), 8.16 (d, J = 8.5 Hz, 1H, H-4), 8.02 (dd, J = 8.5, 1.5 Hz, 1H, H-5), 7.47 (d, J = 8.9 Hz, 2H, H_{ar}), 7.35−7.30 (m, 4H, H_{ar}), 7.17−7.11 (m, 6H, H_{ar}), 7.00 (d, J = 8.9 Hz, 2H, H_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.0, 157.0, 153.4, 149.9, 146.5, 135.8, 133.7, 133.5, 129.6, 127.4, 125.8, 124.5, 124.1, 123.8, 120.7, 111.9, 99.9, 82.4. Anal. Calcd for $C_{28}H_{18}N_2OS$: C 78.11, H 4.21, N 6.51. Found: C 78.30, H 4.10, N 6.45.

*Tris[4-(benzothiazol-6-ylethynyl)phenyl]amine (**T1**).* Eluent hexanes/EtOAc = 3:1; yield 47% (0.22 g); R_f 0.32 (SiO_2, hexanes/EtOAc = 2:1); mp 168−169 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03 (s, 3H, H-2), 8.14 (d, J = 1.2 Hz, 3H, H-7), 8.11 (d, J = 8.5 Hz, 3H, H-4), 7.67 (dd, J = 8.5, 1.2 Hz, 3H, H-5), 7.48 (d, J = 8.6 Hz, 6H, H_{ar}), 7.11 (d, J = 8.6 Hz, 6H, H_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7, 146.8, 134.0, 132.9, 129.7, 125.0, 124.1, 123.5, 120.9, 117.8, 90.2, 88.8 (the number of ^{13}C NMR peaks is reduced due to signal overlapping). Anal. Calcd for $C_{45}H_{24}N_4S_3$: C 75.39, H 3.37, N 7.82. Found: C 75.50, H 3.40, N 7.85.

*Tris[4-(2-formylbenzothiazol-6-ylethynyl)phenyl]amine (**T2**).* Column chromatography on a short pad of silica gel, eluent CH_2Cl_2/MeOH = 20:1; yield 46% (0.24 g); R_f 0.20 (SiO_2, CH_2Cl_2/MeOH = 20:1); mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.17 (s, 3H, CHO), 8.21 (d, J = 8.6 Hz,

3H, H-4), 8.16 (d, J = 1.6 Hz, 3H, H-7), 7.73 (dd, J = 8.6, 1.6 Hz, 3H, H-5), 7.50 (d, J = 8.8 Hz, 6H, H_{ar}), 7.14 (d, J = 8.8 Hz, 6H, H_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.4, 166.1, 153.1, 147.2, 136.9, 133.3, 131.0, 125.8, 125.7, 124.4, 124.1, 117.7, 92.4, 88.9. Anal. Calcd for $C_{48}H_{24}N_4O_3S_3$: C 71.98, H 3.02, N 7.00. Found: C 72.10, H 2.99, N 7.11.

*Tris[4-(benzothiazol-2-ylethynyl)phenyl]amine (**T4**).* Eluent hexanes/EtOAc = 9:1−4:1; yield 59% (0.28 g); R_f 0.32 (SiO_2, MeOH/CH_2Cl_2 = 1:60); mp 259−260 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J = 8.2 Hz, 3H, H_{BTZ}), 7.88 (d, J = 8.2 Hz, 3H, H_{BTZ}), 7.59 (d, J = 8.6 Hz, 6H, H_{ar}), 7.56−7.43 (m, 6H, H_{BTZ}), 7.16 (d, J = 8.5 Hz, 6H, H_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 148.7, 147.6, 135.4, 133.7, 126.7, 126.2, 124.3, 123.6, 121.3, 116.1, 95.8, 83.1. Anal. Calcd for $C_{45}H_{24}N_4S_3$: C 75.39, H 3.37, N 7.82. Found: C 75.45, H 3.31, N 7.79.

*Tris[4-(6-formylbenzothiazol-2-ylethynyl)phenyl]amine (**T5**).* Eluent hexanes/THF = 6:5; yield 42% (0.22 g); R_f 0.57 (SiO_2, hexanes/EtOAc = 2:1); mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.14 (s, 3H, CHO), 8.43 (s, 3H, H_{BTZ}), 8.19 (d, J = 8.5 Hz, 3H, H_{BTZ}), 8.05 (d, J = 8.5 Hz, 3H, H_{BTZ}), 7.62 (d, J = 8.6 Hz, 6H, H_{ar}), 7.18 (d, J = 8.6 Hz, 6H, H_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9, 156.9, 152.9, 147.9, 135.9, 133.99, 133.96, 127.5, 124.4, 124.12, 124.06, 115.8, 98.1, 83.1. Anal. Calcd for $C_{48}H_{24}N_4O_3S_3$: C 71.98, H 3.02, N 7.00. Found: C 72.17, H 3.06, N 7.11.

*General Procedure for Synthesis of **D3**, **D6**, **T3**, and **T6** (Knoevenagel-type condensation).* To a solution of the dipolar (**D2** or **D5**, 0.23 mmol) or the three-branched carbaldehyde (**T2** or **T5**, 0.125 mmol) dissolved in methanol (5 mL) and 2-propanol (12 mL, freshly distilled from CaH_2), respectively, were added malononitrile (1.25 equiv and 3.75 equiv, respectively) and 3−4 drops of pyridine. The reaction mixture was heated to reflux for 2 h, poured into water (30 mL), and extracted with CH_2Cl_2 (4 × 20 mL). The combined organic layers were dried over Na_2SO_4, the solvent was evaporated, and the crude product was purified by chromatography on a short column of silica gel or crystallized from ethanol.

*2-{{6-[(4-Diphenylaminophenyl)ethyn-1-yl]benzothiazol-2-yl}methylene}malononitrile (**D3**).* The crude product was crystallized from ethanol to obtain the target compound as a dark solid in 84% (92 mg) yield. Mp 190−193 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 8.7 Hz, 1H, H-4), 8.11 (d, J = 1.5 Hz, 1H, H-7), 8.08 (s, 1H, CH═C-$(CN)_2$), 7.74 (dd, J = 8.7, 1.5 Hz, 1H, H-5), 7.40 (d, J = 8.9 Hz, 2H, H_{ar}), 7.33−7.27 (m, 4H, H_{ar}), 7.15−7.07 (m, 6H, H_{ar}), 7.02 (d, J = 8.9 Hz, 2H, H_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 152.5, 150.8, 148.9, 147.1, 137.5, 133.0, 131.7, 129.7, 125.5 (2 × C), 125.3, 124.7, 124.2, 121.9, 114.8, 112.9, 111.9, 94.5, 88.2, 87.4. Anal. Calcd for $C_{31}H_{18}N_4S$: C 77.80, H 3.79, N 11.71. Found: C 77.99, H 3.62, N 11.70.

*2-{{2-[(4-Diphenylaminophenyl)ethyn-1-yl]benzothiazol-6-yl}-methylene}malononitrile (**D6**).* Eluent hexanes/EtOAc = 5:1; yield 68% (75 mg); R_f 0.42 (SiO_2, hexanes/EtOAc = 4:1); mp 201−203 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (d, J = 1.8 Hz, 1H, H-7), 8.13 (d, J = 8.6 Hz, 1H, H-4), 7.99 (dd, J = 8.6, 1.8 Hz, 1H, H-5), 7.85 (s, 1H, CH═C$(CN)_2$), 7.48 (d, J = 8.9 Hz, 2H, H_{ar}), 7.35−7.30 (m, 4H, H_{ar}), 7.17−7.11 (m, 6H, H_{ar}), 7.01 (d, J = 8.8 Hz, 2H, H_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 156.8, 154.3, 150.1, 146.4, 136.5, 133.6, 129.6, 129.1, 128.2, 125.8, 124.6, 124.2, 124.1, 120.5, 113.8, 112.8, 111.5, 101.3, 82.5, 82.3. Anal. Calcd for $C_{31}H_{18}N_4S$: C 77.80, H 3.79, N 11.71. Found: C 78.00, H 3.85, N 11.78.

*Tris{4-[2-(2,2-dicyanoethen-1-yl)benzothiazol-6-ylethynyl]phenyl}-amine (**T3**).* Eluent CH_2Cl_2/MeOH = 60:1; yield 45% (53 mg); R_f 0.80 (SiO_2, CH_2Cl_2/MeOH = 60:1); mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, J = 8.6 Hz, 3H, H-4), 8.14 (d, J = 1.5 Hz, 3H, H-7), 8.09 (s, 3H, CH═C$(CN)_2$), 7.75 (dd, J = 8.6, 1.5 Hz, 3H, H-5), 7.51 (d, J = 8.6 Hz, 6H, H_{ar}), 7.14 (d, J = 8.6 Hz, 6H, H_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 152.7, 150.8, 147.3, 137.4, 133.4, 131.7, 125.6, 124.9, 124.8, 124.4, 117.6, 112.8, 111.9, 93.5, 89.0, 87.7. Anal. Calcd for $C_{57}H_{24}N_{10}S_3$: C 72.44, H 2.56, N 14.82. Found: C 72.59, H 2.44, N 14.66.

*Tris{4-[6-(2,2-dicyanoethen-1-yl)benzothiazol-2-ylethynyl]phenyl}-amine (**T6**).* Eluent CH_2Cl_2/MeOH = 60:1; yield 42% yield (50 mg); R_f 0.38 (SiO_2, CH_2Cl_2/MeOH = 60:1); mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (d, J = 1.5 Hz, 3H, H-7), 8.17 (d, J = 8.7 Hz, 3H, H-4), 8.01 (dd, J = 8.7, 1.5 Hz, 3H, H-5), 7.88 (s, 3H, CH═C$(CN)_2$), 7.63 (d, J = 8.7 Hz, 6H, H_{ar}), 7.19 (d, J = 8.7 Hz, 6H, H_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 156.6, 153.7, 147.9, 136.6, 134.1, 129.2, 128.5, 124.4, 124.1, 115.7, 113.6, 112.7, 99.2,83.1, 82.8 (the number of ^{13}C NMR peaks is reduced due to signal overlapping). Anal. Calcd for $C_{57}H_{24}N_{10}S_3$: C 72.44, H 2.56, N 14.82. Found: C 72.64, H 2.41, N 14.71.

2. Two-Photon Absorption Measurements. The two-photon absorption cross-sections, δ_{TPA}, of the dyes were determined via a two-photon excited fluorescence (TPEF) technique using femtosecond pulsed excitation.[8,38] Femtosecond pulses are ideal for this study due to high peak power, capable of inducing nonlinear optical phenomena, combined with low pulse energy. Additionally, the TPEF method is advantageous over other two-photon absorption techniques because the order of the nonlinear absorption can be monitored, avoiding the contribution from excited state absorption or other absorption mechanisms and saturation. A mode-locked Ti:sapphire laser emitting 80 fs pulses tunable from 740 to 850 nm was used as the excitation source. The laser beam was shaped to have a nearly top-hat spatial distribution using a 5-fold beam expander in order to uniformly illuminate a 0.32 NA objective lens used for the excitation of the samples. The TPA-induced fluorescence was collected backward by the same lens and was separated from the excitation beam by using a dichroic mirror and a series of short-pass filters. Finally, it was detected by a photomultiplier connected to photon-counting electronics. The TPA fluorescence intensity was measured as a function of the excitation power every 10 nm within the wavelength range of the excitation laser. In all cases, the calculations of δ_{TPA} were made within the power regime, where the fluorescence was proportional to the square of the excitation power, in order to ensure that the observed fluorescence was only due to two-photon absorption. The samples were measured as 1×10^{-5} M solutions of the dyes in toluene. In a reference experiment, the scattered light from a cuvette with toluene was measured, through the same setup, as a function of excitation power. This signal was consequently subtracted from the TPA fluorescence signal of the dyes. The values of δ_{TPA} were determined using rhodamine B (1×10^{-4} M in methanol) as a reference, which has a well-known TPA spectrum. For the calculation of δ_{TPA}, it was assumed that the fluorescence quantum yield is the same under two-photon or one-photon excitation following the analysis of Xu et al.[39]

3. Computational Details. The ground-state structures of push−pull triphenylamines containing a benzothiazole subunit were fully optimized at the DFT level employing the B3LYP[40] functional and TZVP[41] basis set with the Turbomole program.[42] The time-dependent DFT method with the 6-31G(d) basis set and the Coulomb-attenuated CAM-B3LYP[43] exchange-correlation functional, as implemented in the Gaussian 09 program package,[44] was applied to get excitation energies (E_{max}), transition dipole moments (μ_{01}), oscillator strengths (f_{osc}), and adiabatic dipole moment changes ($\Delta\mu_{01}$) between the ground state and the first excited state. Solvent effects were simulated by employing a polarizable continuum model (PCM).[18,45]

The TPA cross-sections δ_{TPA} were evaluated by calculating the two-photon transition moment matrix elements $S_{\alpha\beta}$ in the Dalton program.[46,47] With the $S_{\alpha\beta}$ elements in hand, the TPA cross-section of the molecule for linearly polarized monochromatic light was calculated (in atomic units) as:

$$\delta_{a.u.} = \frac{1}{30}\sum_{\alpha,\beta}(2S_{\alpha\alpha}S^*_{\beta\beta} + 4S_{\alpha\beta}S^*_{\beta\alpha})$$

The final expression for the TPA cross-section, which is directly comparable to experiment, was used

$$\delta_{TPA} = \frac{(2\pi)^3 \alpha a_0^5}{c}\frac{\omega^2}{\pi\Gamma}\delta_{a.u.}$$

Here, α is the fine structure constant, a_0 the Bohr radius, c the speed of light, ω the energy of the exciting photon (in case of the TPA process, one-half of the excitation energy), and $\pi\Gamma$ a normalization factor due to the Lorentzian line-shape broadening of the excited state (Γ =0.2 eV was assumed throughout this work). The units of δ_{TPA} will become GM ($cm^4 \cdot s \cdot photon^{-1}$), provided we use centimeter-gram-second units for a_0 and c, and atomic units for ω and Γ.

■ ASSOCIATED CONTENT

Supporting Information. General experimental methods, ^1H and ^{13}C NMR spectra of new compounds, linear and nonlinear optical properties of dipolar compounds calculated at the DFT level, and Cartesian coordinates of the optimized ground-state structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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