Molecular Structure – Optical Property Relationships for a Series of Non-Centrosymmetric Two-photon Absorbing Push-Pull Triarylamine Molecules

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This article reports on a comprehensive study of the two-photon absorption (2PA) properties of six novel push-pull octupolar triarylamine compounds as a function of the nature of the electron-withdrawing groups. These compounds present an octupolar structure consisting of a triarylamine core bearing two 3,3⁹-bis(trifluoromethyl)phenyl arms and a third group with varying electron-withdrawing strength (H, CN, CHO, NO₂, Cyet, Vin). The 2PA cross-sections, measured by using the femtosecond open-aperture Z-scan technique, showed significant enhancement from 45 up to 125 GM for the lowest energy band and from 95 up to 270 GM for the highest energy band. The results were elucidated based on the large changes in the transition and permanent dipole moments and in terms of (i) EWG strength, (ii) degree of donor-acceptor charge transfer and (iii) electronic coupling between the arms. The 2PA results were eventually supported and confronted with theoretical DFT calculations of the two-photon transition oscillator strengths.

Comprehensive studies of the two-photon absorption (2PA) cross-section on a wide spectral range are of fundamental importance to understand, at the molecular level, the relation between the molecular structure and electronic and optical properties of novel organic materials. Due to its remarkable characteristics, such as the advantageous excitation in the near-IR region and the high spatial localization of excitation, the 2PA has been used in several kinds of applications including 3D optical data storage, fluorescence imaging, all-optical switching, optical power limiting, photodynamic therapy, frequency upconverted lasing, coherent control of molecular systems, microfabrication via photopolymerization, micromachining, to name a few.

In the last three decades, different types of molecules have been proposed as alternative molecular designs to improve nonlinear hyperpolarizabilities and decrease the irradiance threshold necessary to generate a specific nonlinear optical effect. Three main designs have been largely studied: the dipolar (A–p–D), quadrupolar (A–p–D–p–A), and octupolar structures (D–p–A), where D and A refer to the electron-donating and electron-withdrawing groups respectively, linked through a bridge of π-conjugated bonds. On the other, some authors also followed the oligomeric strategy and explored the possibility of designing organic molecules exhibiting at the same time a strong 2PA and a good transparency. Recently, great efforts have been focused...
on the synthesis of octupolar structures since they have demonstrated strong electronic coupling between the individual arms, giving rise to prodigious hyperpolarizabilities. Moreover, as it has been shown by some of us, for octupolar molecules whose permanent dipole moment vanishes in the gas phase, aggregation can still take place due to the thermal motions of atoms and strong intermolecular interactions.

Among the octupolar structures, push-pull triarylamine compounds stand out due to their good electron donating and transporting capability. Thereby, their noteworthy electronic and optical properties have been harnessed in different applications as active layers for two-photon holographic rewritable micropatterning, fluorescence photoswitching, or dye-sensitized solar cells. However, for most of the triarylamine compounds reported so far, the overlap of the π molecular orbitals (MOs) carrying the nitrogen lone pair with the π MOs on the phenyl rings is relatively poor due to the large dihedral angle between the planes containing the phenyl ring on one side and the nitrogen-bonded carbon atoms on the other side, hence the 2PA performances were severely impaired. We want here to investigate the influence of the introduction in the positions 3 and 5 of the phenyl rings of electron-withdrawing groups such as the trifluoromethyl (CF3) one, and the distinct strength of the electron-withdrawing groups (H < CN < CHO < NO2 < Cyet < Vin) upon the 2PA property of triarylamine derivatives. Furthermore, the CF3 group imparts organic molecules with hydrophobic properties which exert positive influence on their use as biologically active compounds. In this context, we reported here a comprehensive experimental and theoretical study on the 1PA and 2PA properties of six push-pull triarylamine molecules containing trifluoromethyl (CF3) and distinct electron-withdrawing groups (EWG). Since these molecules present octupolar structures with phenyl bridges and strong electron-donating (triarylamine) and electron-accepting (trifluoromethyl) groups, large changes in dipole moment upon excitation are expected. Presumably, the presence of the CF3 may result in enhanced charge transfer from the amino core toward the CF3-biphenyl groups in one of the excited states. For the 2PA measurements, we employed the open-aperture Z-scan technique using an optical parametric amplified pumped by a femtosecond laser system operating at a low repetition rate (1 KHz). Two and three-energy level approximations helped us establish a quantitative relationship between the 2PA and the molecular properties of the chromophores in solution. This relationship is established by comparing the values of the transition dipole moments μ and dipole moment changes Δμ obtained from 2PA and solvatochromic shift measurements. The results were also compared with theoretical predictions of the one- and two-photon transitions strengths, transition dipole moments and dipole moment changes upon excitation, provided by response function calculations within the density functional theory (DFT) framework. Linear optical properties such as molar absorptivity, one-photon induced fluorescence, transition and permanent dipole moments, fluorescence quantum yields and lifetimes also are reported.

Results

Synthesis of the push-pull triarylamine compounds. The synthesis of the targeted compounds proceeded via a Suzuki aromatic coupling reaction between the commercially available 3,5-bis(trifluoromethyl)phenylboronic acid and various bis(4-bromophenyl)phenylamino derivatives differing by the nature of their electron-withdrawing group (Figure 1). In this way, four derivatives CF3X where X = H, CN, CHO and NO2 could be obtained as white to bright yellow solids. The last two derivatives CF3Cyet and CF3vin were issued from an additional Knoevenagel reaction between CF3CHO and ethyl cyanoacetate and malononitrile respectively, assisted by ammonium acetate as an acidic catalyst in a solvent mixture of pyridine:acetic acid (10:1). The compounds appear as bright orange-yellow solids. All six compounds were carefully purified by chromatography column before studies.

One-photon absorption and emission, oxidation potentials. The ground-state absorption and emission spectra of the push-pull triarylamine derivatives CF3EWG are illustrated in Fig. 2a and 2b, respectively. All molecules present an intense absorption band in the UV range around 350–370 nm. A second absorption band appears at lower energy in the visible range for compounds CF3NO2, CF3Cyet and CF3vin. Interestingly, compared to their homologous derivatives tBuEWG, substituted by electron-donating tert-butyl groups the para-phenyl position the CF3EWG series, substituted by two electron-withdrawing trifluoromethyl groups in the meta positions, exhibit bathochromic and hypsochromic shifts of their UV and visible

Figure 1 | Synthetic pathway toward the octupolar push-pull triarylamine compounds CF3EWG: i-; 3,5-bis(trifluoromethyl)phenylboronic acid, Pd(PPh3)4, Na2CO3, 2 mol. L−1, toluene, 80 °C, 8 h; ii- ethyl cyanoacetate or malononitrile, pyridine:acetic acid (10:1), NH4OAc, RT, 6 h.
absorption bands respectively. However, their molar absorption coefficients \( \varepsilon \) are similar to those obtained for the tBuEWG series.41,42

As for the absorption spectra, only one fluorescence band is observed in the visible region. Interestingly, two kinds of photophysical behaviors can be distinguished. The first one relates to compounds CF3NO2, CF3Cyet and CF3vin. All three display an emission band centered around 430 nm and similar Stokes shifts ranging from 4300 to 5100 cm\(^{-1}\). As already discussed for the tBuEWG series, femtosecond transient absorption spectroscopy measurements showed that the compounds underwent a significant nuclear rearrangement in the excited state after a charge transfer occurred from the triphenylamino core onto the EWG unit. The second behavior is described by compounds CF3H, CF3CN and CF3CHO which exhibit an emission band centered around 430 nm and similar Stokes shifts ranging from 4300 to 5100 cm\(^{-1}\). Compared to the other two compounds, the emission band of CF3CHO lies at lower energy in accordance with the more red-shifted wavelength of the corresponding maximum absorption. Finally, the emission of CF3H in toluene located at 428 nm instead of 383 nm for the tBuH homologue shows a clear participation of the trifluoromethyl groups in the radiative excited state and presumably in the Franck-Condon state also.

The electronic influence of the CF3 groups is clearly apparent in the oxidation of the triphenylamino core into a triphenylammonium cation as featured by the first redox potential (Table 1). All triarylamine derivatives CF3EWG examined in this study displayed a quasi-reversible process characterized by an averaged redox potential \( E^0 \) ranging from 0.63 to 0.87 V (vs Fc\(^+/\)Fc depending on the EWG substituents). Compared to the series of electron-donating compounds tBuEWG, the \( E^0 \) values rise by 0.17 to 0.2 V. This considerable increase, being much more significant for CF3H, is to be ascribed to the electron-deficient character of the CF3 groups, thus decreasing considerably the electron density located on the triphenylamino core in the ground state. No simple correlation between the electrochemical measurements and the optical gaps could however be traced, which is due to the high sensitivity of the excited state on the solvent polarity as it will be discussed later.

**Character of electronic transitions and solvatochromic measurements.** In order to investigate the nature of the transitions observed along the 1PA spectra, we performed the analysis of response vectors to determine the largest one-electron orbital excitations. As it can be noted in Fig. 3, the lowest-energy transition for the H and CN derivatives is a \( \pi \rightarrow \pi^* \) transition involving the trifluoromethyl-phenyl arms (acceptor groups). For all other compounds, the lowest-energy transition is an ICT transition involving the triarylamino core and the respective EWG. The reason for this ordering difference stems in the low strength of the CN substituent, which therefore does not promote the inversion between the \( \pi^* \) and ICT excited states as observed for all the other substituents. The influence of the EWG strength on this inversion is also evidenced by the

![Figure 2](image-url) | (a) Ground-state absorption and (b) fluorescence spectra of push-pull triarylamine derivatives containing CF3 in toluene solutions.

| Table 1 | UV-vis absorption and emission properties in toluene solution |
|----------|---------------------------------------------------------------|
| ![Image](image-url) |
| ![Table](table-url) |
molecular orbital involved in the excitations of the CHO substituent. Because of its moderate EWG strength, the charge transfer from the triarylamine core to the EWG in the case of CHO substituent is not as pronounced as for the NO2, Cyet and Vin substituents.

To shed more light on the character of electronic transitions, we performed solvatochromic Stokes shift measurements to find the difference between the permanent dipole moments in the excited and ground states, \( D_{\text{SS}} \). For this purpose, we used the Lippert-Mataga equation:

\[
D_{\text{SS}} = \frac{3\pi \hbar c D}{4} \frac{\partial \tilde{u}}{\partial F} \frac{1}{F} \text{Vol}
\]

where \( \tilde{u} = u_A - u_m \) is the difference between the wavenumbers of the maximum absorption and fluorescence emission (in cm\(^{-1} \)), \( F(n, \tilde{\zeta}) = 2(\tilde{\zeta} - 1)/(2\tilde{\zeta} + 1) - 2(n^2 - 1)/(2n^2 + 1) \) is the Onsager polarity function with \( \tilde{\zeta} \) being the dielectric constant of the solvent, Vol is the volume of the effective spherical cavity occupied by the molecule inside the dielectric medium. Various solvents or mixtures of solvents (cyclohexane, hexane, toluene, hexane/chloroform (50/50%), hexane/dichloromethane (50/50%), chloroform, dichloromethane, acetone and ethanol) with increasing polarity were investigated for all compounds.

A pronounced increase of the Stokes shift was found with increasing solvent polarity and reveals clearly the polar character of the radiative excited state (S\(_1\)) (Fig. 4). These results indicate that the absolute values of the excited state dipole moments \( \tilde{\mu}_{\text{SS}} \) are much higher than those of the ground state dipole moments \( \tilde{\mu}_{00} \).

From the Fig. 4, we found \( \frac{\partial \tilde{u}_{\text{OH}}}{\partial F} = 3280 \pm 730 \text{cm}^{-1} \), \( \frac{\partial \tilde{u}_{\text{CN}}}{\partial F} = 2340 \pm 165 \text{cm}^{-1} \), \( \frac{\partial \tilde{u}_{\text{CHO}}}{\partial F} = 2420 \pm 160 \text{cm}^{-1} \), \( \frac{\partial \tilde{u}_{\text{NO}}}{\partial F} = 3930 \pm 350 \text{cm}^{-1} \), \( \frac{\partial \tilde{u}_{\text{Cyet}}}{\partial F} = 5150 \pm 510 \text{cm}^{-1} \) and \( \frac{\partial \tilde{u}_{\text{Vin}}}{\partial F} = 5220 \pm 780 \text{cm}^{-1} \). Using these data, the hydrodynamics volume estimated from the IEF-PCM/B3LYP/631G(d,p) calculations (see Table 1) and the Eq. 3, we found \( D_{\text{SS}} \) values (between 9 to 15 Debye) indicating a high degree of effective charge transfer (>34%), which can be obtained from the relation \( r_{\text{eff}} = |\Delta \mu|/e \), where \( e \) is the electron charge. Table 1 reports the degree of charge transfer observed for all molecules.

As one can note, the degree of ICT (\( r_{\text{eff}}/r \)), where \( r \) is the distance between the core and the first EWG atom obtained from the DFT calculations, for the molecules CF\(_3\)CN and CF\(_3\)CHO is considerably smaller than that of CF\(_3\)H, even though the cyano and aldehyde substituents have a higher EWG strength. Another important outcome that we can infer from these results is the increase in the degree...
of ICT caused by higher splitting of the lowest energy 1PA band. The splitting in quasi-degenerate excited states is a result of the interactions between the arms of the chromophores. Whereas no such splitting could be experimentally distinguished for CF3CN and CF3CHO that have the lowest values of ICT, clear interactions could be noticed for the other four compounds: a shoulder on the lowest energy band for CF3H with an energetic separation of \( \sim 300 \) meV, and a considerable splitting for CF3NO2 (\( \sim 460 \) meV), CF3Cyet (\( \sim 610 \) meV) and CF3Vin (\( \sim 740 \) meV). We used the Gaussian decomposition method to estimate the splitting energy for CF3CN and CF3CHO and obtained 240 meV and 250 meV, respectively. From these values and based on the exciton Frenkel model, we estimated the electronic coupling constant for all octupolar structures as being \( \sim 100 \) meV for CF3H, \( \sim 80 \) meV for CF3CN and CF3CHO, \( \sim 155 \) meV for CF3NO2, \( \sim 205 \) meV for CF3Cyet and \( \sim 245 \) meV for the CF3Vin. As a conclusive point, our results show that the electronic coupling is directly proportional to the degree of ICT of EWG.

Table 1 also reports the photophysical parameters of push-pull triarylamine derivatives containing CF3, such as: maximum absorption and fluorescence wavelengths, maximum molar absorptivity, and, moreover, very strict. However, in compounds that present a low molecular symmetry, so that it is not possible to define the parity of excited states precisely, the same electronic state may be accessed via both one and two-photon absorptions.

It is worth mentioning that, for all molecules, the highest energy 2PA band has the highest cross-section values that are between 95 GM (for CF3H) to 270 GM (for CF3Vin). This band is associated with electronic states that present high 2PA probability located in the UV region (from 260 nm to 300 nm).

The cross-section values, at the peak of the main 2PA bands, were determined to be c.a.65 GM at 725 nm, 83 GM at 620 nm and 97 GM at 520 nm for CF3H; 58 GM at 715 nm and 145 GM at 560 nm for CF3CN; 48 GM at 720 nm and 262 GM at 580 nm for CF3CHO; 45 GM at 800 nm, 58 GM at 680 nm and 230 GM at 585 nm for CF3NO2; 115 GM at 850 nm, 68 GM at 700 nm and 250 GM at 610 nm for CF3Cyet; 125 GM at 880 nm; 70 GM at 700 nm and 265 GM at 605 nm for CF3Vin. The 2PA cross-section values reported here for the triarylamine molecules containing CF3 are at least 30% higher than those reported for their tert-butyl analogues. However, we cannot attribute this 2PA enhancement to the CF3 groups because this difference may be associated only with the higher polarity of solvent used in this present report (toluene) when compared to the results of Refs. The primary reason is that the experimental 2PA spectra do not exhibit a fine vibrational structure for the absorption bands. However, in the case of multi-branched structures, vibronic contributions to the two-photon absorption may be substantial. It is important to mention that two-photon transitions are different from the one-photon ones and, moreover, very strict. However, in compounds that present a low molecular symmetry, so that it is not possible to define the parity of excited states precisely, the same electronic state may be accessed via both one and two-photon absorptions.

Experimental 2PA properties. Figure 5 shows the experimental 2PA spectra (dots) determined by performing open-aperture Z-scan measurements with femtosecond pulses. The experimental data reveal well-defined 2PA spectra with moderate cross-section values from several tens to few hundreds of GM units) in the visible and infrared regions depending on the electronic influence of the withdrawing substituents.

Along the 2PA spectra we can distinguish, except the molecules with the lowest degree of ICT (CF3CN and CF3CHO), three 2PA allowed bands and the resonance enhancement effect. Among the three 2PA bands, those two ones of lower energy are related to the ICT (S0→S1) transition and the π→π* (S0→S2) transition located on the trifluoromethyl-phenyl arms in agreement with the linear absorption spectra. This assumption is supported by the good spectral correspondence observed between the bands in the 2PA and 1PA spectra (see Fig. 5) and also by the results of the response function calculations (see theoretical results section). Slight blue shifts between the spectral position of 1PA and 2PA peaks may be ascribed to the distinct vibronic coupling between the ground- and excited-states in the 1PA and 2PA transitions. Although the computational strategies to include vibronic coupling are well established, we have not attempted to apply them in the present study.
transition dominate the nonlinear optical effect in this region. This result can be attributed to the low electronic coupling constant observed for these molecules (~80 meV).

For the other molecules, as it was observed in the 1PA spectra, the 2PA spectra exhibit a clear and increasing (in energy) splitting of the lowest energy band as a function of increase of the degree of ICT. Our results point out that for CF$_3$H ($\sigma_{S2}^{2PA}/\sigma_{S1}^{2PA} = 1.3$) and CF$_3$NO$_2$ ($\sigma_{S2}^{2PA}/\sigma_{S1}^{2PA} = 1.2$), the $\pi-\pi^*$ ($S_0\rightarrow S_2$) transition has higher 2PA cross-section values than that of the corresponding $S_0\rightarrow S_1$ transition, whereas for CF$_3$Cyet ($\sigma_{S2}^{2PA}/\sigma_{S1}^{2PA} = 0.59$) and CF$_3$Vin ($\sigma_{S2}^{2PA}/\sigma_{S1}^{2PA} = 0.56$) the opposite is found. This result can be at least partially explained due to the lower transition dipole moment ($|\mu_{01}|$), observed for CF$_3$H and CF$_3$NO$_2$ as compared to CF$_3$Cyet and CF$_3$Vin. In the context of the sum-over essential states approach, the 2PA cross-section of the lowest energy transition, which is proportional to the product of $|\mu_{01}|^2$ and $|\Delta\mu_{01}|^2$, became less intense.

Since the 2PA cross-section of the $S_0\rightarrow S_2$ transition for CF$_3$H is the highest one despite a larger ICT encountered for the other octupolar compounds CF$_3$NO$_2$, CF$_3$Cyet and CF$_3$Vin, one can suspect for CF$_3$H a large electronic coupling between its bis(trifluoromethyl)biphenyl arms upon 2PA excitation. The lower 2PA cross-sections for CF$_3$NO$_2$, CF$_3$Cyet and CF$_3$Vin molecules may be due to increased angular torsions of the NO$_2$, Cyet and Vin substituents around the phenyl-N bonds, thus leading to a reduced electronic coupling between the arms and, as a consequence, a decrease in the 2PA cross-section of $S_0\rightarrow S_2$ electronic transitions.

To establish a more quantitative relationship between the effect of distinct EWG and the observed 2PA activity, we used the sum-over-essential states approach to determine the permanent dipole moment change between the ground and excited states and the transition dipole moments between excited states. Details about this approach can be found in “Supporting information”. Figure 6 shows a comparison between the $|\Delta\mu_{01}^{2PA}|$ values obtained from 2PA and
solvatochromic shift measurements. As it can be observed in Fig. 6, there is a good agreement between the results determined from 2PA and solvatochromic shift measurements. These results show that the lowest-energy 2PA band for all molecules can be well-described by a two-level system.

To model the $S_0\rightarrow S_2$ 2PA allowed transition, we considered a three-level system composed of the ground state ($S_0$), one intermediate 1PA allowed excited state ($|1\rangle$) and the 2PA allowed final excited state ($S_2$). Table 1 shows the results obtained using the methodology described in “Supporting information”. The main aspect to be highlighted, based on these results, is that upon going from the neutral substituent (H) to the strongest EWG (Vin), the transition dipole moment that connects the two lowest energy 2PA allowed states, $|\mu_{12}\rangle$, decreases by about 2.5–5 times, due to the influence of the EWG on the electronic coupling between the arms of the octupolar structure. For CF$_3$CN and CF$_3$CHO, a decrease in the transition dipole moment $|\mu_{12}\rangle$ was expected since these molecules present lower electronic coupling constant as compared to CF$_3$H. For the other molecules, the NO$_2$, Cyet and Vin substituents should increase the angular torsion of the whole plane phenyl-EWG along the N-phenyl bond, which impairs electronic coupling between the arms, thus decreasing $|\mu_{12}\rangle$. In this context, the structure–property relationships outlined in this study are of foremost importance for the development of novel organic materials with remarkable nonlinear optical properties.

**Theoretical results.** In what follows, we present the results of quantum-chemical calculations of the electronic structures of triarylamines using response functions. The data presented in Table 2 correspond to the results of calculations performed using reparametrized CAM-B3LYP functional and some additional information extracted from the experimental data. In general, a satisfactory agreement between the transition energies determined by the response function calculations and through the theoretical fitting of the experimental 1PA spectrum is observed. The difference found for the lowest energy transition $S_0\rightarrow S_1$ is smaller than 0.15 eV for all molecules. In the case of the second transition reported in Table 2, $S_0\rightarrow S_{n=2,3}$, the difference observed is smaller than 0.18 eV basically for all molecules, the only exception (0.26 eV) being the case of Cyet substituent.

The states accessed via two-photon transitions are also allowed via one-photon transition as shown by the reasonable oscillator strength obtained for all the transitions (see Table 2). Such results confirm that the electric-dipole selection rules are relaxed for all the compounds investigated, which was expected due to the absence of centrosymmetric.

By comparing the results of the gas-phase (not shown) and PCM calculations, the solvent effects promote a red-shift and the increase in the oscillator strength for all transitions, the only exception being the second transition of Cyet substituent that shows a small blue-shift. In addition, the comparison shows that the solvent effects promote a 2PA probability increase for all the transitions of the investigated substituents. The solvent effects increase the 2PA probability by about 80–130%. To better compare the experimental data and theoretical results for 2PA process, we simulated the 2PA cross-section spectrum of the triarylamines molecules by using the excited state linewidths estimated by fitting the experimental linear spectra and the 2PA transition probabilities determined by the quadratic response calculations (see Table 2). The simulated and experimental 2PA cross-section spectra are presented in Figure 7. As it can be seen, there is a good agreement between the simulated and experimental spectra both for the spectral behavior and cross-section magnitude.

For each investigated molecule, the simulated 2PA cross-section spectrum reproduces the bands observed over the experimental spectrum. The magnitude of the 2PA cross-section at the peak of each absorption band observed in the experimental spectrum and the related value in the simulated spectrum are gathered in Table 2.

**Discussion**

The experimental 2PA cross-sections observed along the nonlinear optical spectra for the CF$_3$EWG molecules as a function of the nature of the electron-withdrawing group can be explained from the competition among the EWG strength, the degree of donor-acceptor charge transfer and the electronic coupling among the arms present in each molecule. Based on these parameters, our experimental results showed that the Cyet and Vin substituents favors the first 2PA band (which has the ICT character) in detriment to their second band due to the poor electronic coupling between the arms and the strong donor-acceptor (N→EWG) charge transfer. However, CF$_3$Cyet and CF$_3$Vin have an electronic coupling constant higher than those observed in the case of CF$_3$H and CF$_3$NO$_2$ which present 2PA cross-sections higher to the second 2PA band as compared with the first one. Nevertheless, in solution, the octupolar CF$_3$Cyet and CF$_3$Vin molecules present a considerable increase in angular torsions of the whole plane phenyl-EWG along the N-phenyl bond that lead to a reduced electronic coupling between the arms, thus decreasing the 2PA cross-section of the $S_0\rightarrow S_1$ electronic transition. These angular torsions were recently observed through femtosecond transient absorption spectroscopy measurements for similar molecules. On the other hand, for CF$_3$CN and CF$_3$CHO, the fact of the $S_0\rightarrow S_1$ transition dominates the lowest energy 2PA band (at least 70%) is due exclusively to the low electronic coupling constant observed for these molecules (≈80 meV).

All CF$_3$EWG molecules present the highest energy 2PA band with the highest cross-section value which ranges from 95 GM for CF$_3$H to 270 GM for CF$_3$Vin. This band is associated with an intense electronic transition that present high 2PA probability located in the UV region (from 260 nm to 300 nm) as well as the resonance enhancement effect due to the little detuning between the excitation energy and the energy of the lowest energy one-photon allowed state.

By comparing the magnitude of the 2PA cross-section of the two lowest energy transitions, the theoretical results and experimental data show a nice match, i.e. in the case of the H and NO$_2$ substituents the higher energy transition presents a larger cross-section. For the remaining substituents, the theoretical results and experimental data do not agree about which transition presents the higher 2PA cross-section. At least two factors may dramatically affect the agreement between the theoretical results and experimental data. In the case of the CN and CHO substituents the two-lowest energy transitions are close in energy, as evidenced by the theoretical results and
the structureless band observed in their 1PA spectrum. In such a situation, the accuracy of the procedure to fit the experimental linear spectra and estimate the spectral linewidth of the related excited states, which is then used to compute the 2PA cross-sections, cannot be completely reliable. Since for the CN and NO2 substituents, the 2PA transition probability of the two lowest energy transitions are roughly similar, an accurate estimative of the linewidth of the excited state is crucial to determine which transition presents the higher probability. For the Cyet substituents, on the other hand, the two-lowest energy transitions are separated in energy and, therefore, the estimated values of the spectral linewidths are more reliable. Also, the 2PA probabilities of the two lowest energy transitions are quite different for these substituents. In order to find a reliable cross-section of the 2PA transition, one can observe that the trifluoromethyl groups do not take part in such a transition.

**Methods**

**Compounds.** All chemical reagents and solvents were purchased from commercial sources (Aldrich, Acros, SDS) and used as received. Spectroscopic grade solvents purchased from Aldrich were used for spectroscopic measurements. Bis(4-bromophenyl)phenylamine, 4-di(4-bromophenyl)aminobenzonitrile, 4,4-di(4-bromophenyl)aminobenzaldehyde and bis(4-bromophenyl)-4-nitrophenylamine were synthesized according to previous reported procedures. Details about the synthesis for the CF3H, CF3CN, CF3COH, CF3NO2, CF3Cys, CF3Vin molecules can be found in “Supporting information”.  

**Electrochemical measurements.** Electrochemical measurements were performed with a three-electrode cell consisted of a glassy carbon working electrode (1.5 mm diameter), a counter electrode made of a Pt wire coil and an Ag/AgCl reference electrode. The Ag/AgCl reference electrode was obtained by introducing a silver wire in the reference compartment containing silver ions (AgNO3, 0.1 M) and tetrabutylammonium perchlorate (TBAP, 0.1 M) in acetonitrile. The measured redox potential were expressed vs ferrocene used herein as internal reference. The triarylamines were prepared in dichloromethane solvent added with 0.1 M of tetrabutylammonium hexafluorophosphate (Bu4NPF6) as a supporting electrolyte (Sigma-Aldrich). The solutions were deoxygenated by argon bubbling prior to each experiment. Cyclic voltammograms (CVs) were performed with VSP potentiostat controlled by EC-Lab 10.02 software. Both potentiostat and software were purchased from Bio-Logic Instruments-France.

| Compound | E° (V) vs Ag/AgCl | E° vs Ag/AgCl | ΔE (V) | ΔE (V) | ΔE (V) | ΔE (V) | ΔE (V) | ΔE (V) | ΔE (V) | ΔE (V) | ΔE (V) |
|----------|------------------|--------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| CHO      | 1.20             | 1.10         | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   |
| Cyet     | 1.10             | 1.00         | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   |
| NO2      | 1.00             | 0.90         | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   |
| CHO      | 1.20             | 1.10         | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   |
| Cyet     | 1.10             | 1.00         | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   |
| NO2      | 1.00             | 0.90         | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   | 0.10   |

The nonlinear optical properties were measured by using the open aperture Z-scan technique, employing 120-fs laser pulses from an optical parametric amplifier pumped by 150-fs pulses (775 nm) from a Ti:sapphire chirped pulse amplified system. The Z-scan measurements were carried out with intensities ranging from 60 to 200 GW/cm² (30 to 120 nJ/pulse) and with beam waist size at the focus varying from 15 to 18 μm. To ensure a Gaussian profile for the laser beam used in the experiments, spatial filtering is performed before the Z-scan setup. A silicon detector was employed to monitor the laser beam intensity in the far-field. To improve the signal to noise ratio, the oscillatory Z-scan method was used such that the samples are continuously scanned, repeating the experiment several times.
Moreover, a lock-in amplifier served to integrate 1000 shots for each point of the Z-scan signature. In the open aperture Z-scan technique, 2PA cross-section was determined by translating the sample through the focal plane of a focused Gaussian beam, while transmittance changes in the far field intensity are monitored. For a 2PA process, the light field created an intensity dependent absorption, \( I = I_0 + \beta I \), in which \( I \) is the linear absorption coefficient, \( I_0 \) is the laser beam intensity, and \( \beta \) is the 2PA coefficient. The nonlinear coefficient \( \beta \) was obtained by fitting the Z-scan data. The 2PA cross-section, \( \sigma_{2PA} \), was determined from

\[
\sigma_{2PA} = \frac{vb}{N},
\]

where \( v \) is the excitation photon energy, and \( N \) is the number of chromophores per cm\(^3\). The 2PA cross-section was expressed in Goëppert-Mayer (GM) units, where 1GM = 1 \( \times \) 10\(^{-46}\) cm\(^2\) s photon\(^{-1}\).

Fluorescence quantum yield and time resolved measurements. Steady-state emission spectra were recorded using a Perkin Elmer LS55 or a Fluoromax 3 (Horiba-Jobin-Yvon) spectrophotometers respectively. Fluorescence intensity decays were measured by the time-correlated single-photon counting method (TCSPC) with a femtosecond laser excitation at 340 or 400 nm provided by a Spectra-Physics setup composed of a Titanium-Sapphire Tsunami laser pumped by a doubled YAG laser (Millenia), pumped itself by a two-laser diode array, and doubling and tripling LBO crystals. Light pulses were selected by optoacoustic crystals at a repetition rate of 4 MHz. Fluorescence photons were detected at the emission maximum through a monochromator by means of a Hamamatsu MCP R3809U photomultiplier, connected to a constant-fraction discriminator. The time-to-amplitude converter was from Tennelec. Pulse deconvolution was performed from the time profile of the exciting pulse recorded under the same conditions by using a Ludox solution. The fluorescence data were analyzed by a nonlinear least-squares global using the Globals software package developed at the Laboratory for Fluorescence Dynamics at the University of Illinois at Urbana-Champaign (Globals software, Irvine, CA, USA).

Computational details. In this paper, quantum chemical calculations were employed to investigate the molecular and electronic structures of triarylamine molecules containing trifluoromethyl and determine their one-photon and two-photon transitions and related electronic structure parameters. For this purpose, quantum chemical calculations using the Kohn-Sham formulation of density functional theory (KS-DFT) were performed. The equilibrium molecular geometry of the molecules was determined in both gas-phase and solvent environment. The solvation effects on the equilibrium molecular geometry, the electronic structure and the one-photon and two-photon properties of each investigated molecule were taken into account by employing a Polarizable Continuum Model (PCM) and assuming the toluene solvent.

The gas-phase geometry optimizations were performed employing the B3LYP/6-311G(d,p) approach. In the case of the geometry optimization taking into account the solvent environment, the PCM using the integral equation formalism variant (IEF-PCM) was employed in combination with the B3LYP/6-311G(d,p) approach. All the geometry optimizations were performed using the United Atom for Hartree-Fock (UAHF) model to build the solute cavity. In this model the van der Waals surface is constructed from spheres located on heavy (that is, non-hydrogen) atoms only (United Atom approach). The van der Waals radius of each atom is a function of atom type, connectivity, total charge of the molecule and the number of attached hydrogen atoms. The hydrodynamic volume of each molecule in toluene was theoretically determined from the PCM-B3LYP/6-311G(d,p) calculation. These theoretical values were used to estimate the permanent dipole moment changes under excitations based on experimental data.

**Figure 7** | The dots represent the experimental 2PA cross-section spectra. The solid lines correspond to the simulated 2PA cross-section spectra obtained using the 2PA transition probabilities determined by the response function calculations and excited states linewidths estimated by fitting the experimental nonlinear spectra using the sum-over essential states approach.
To determine the lowest energy one- and two-photon allowed transitions and related molecular parameters of the investigated molecules, the response function calculations within the DFT framework were performed using the DALTON program. In this approach, the excitation energies and transition dipole moments (two-photon probabilities) are analytically computed, respectively, poles and single residues of the linear (quadratic) response function of the electronic transition density. Moreover, by computing the double residue of the quadratic response function the excited states dipole moments and the transition dipole moment between excited states were also determined. All the response function calculations were performed employing the CAM-B3LYP/6-31 + G(d) approach for the investigated molecules in both gas-phase and solvent environment. In the case of the response function calculations, the PCM as implemented in DALTON program was employed. To be consistent, for all molecules the van der Waals surface used in the response function calculations was defined by adopting the set of van der Waals radius and atomic centers determined at the geometry optimization stage using the Gaussian 2009 package.

A preliminary assessment of the exchange-correlation functionals revealed that the standard hybrid B3LYP and PBE0 functionals and also the standard long-range corrected CAM-B3LYP functional, fail to well reproduce the experimental UV–vis spectra of the triarylamine molecules containing trifluoromethyl investigated (for a recent exhaustive summary of TD-DFT benchmarks we refer to excellent reviews). Therefore, in this study the successful strategy of K. Okuno et al. of employing a tuned CAM-B3LYP functional was employed. In their systematic study, K. Okuno et al. showed that the use of the time-dependent density functional theory (TD-DFT) scheme with the tuned CAM-B3LYP functional is found to semi-quantitatively reproduce several excitation energies identified from the experimental UV–vis spectra of 15 closed forms of diarylethene derivatives. In that study, the default value of the CAM-B3LYP functional parameters, that is, \( \alpha = 0.33, \beta = 0.46, \) and \( \delta = 0.0799 \) were used. The TD-DFT calculations were performed assuming the gas-phase condition. In the present study the values of the functional parameters were defined based on the comparison between the energy of the one-photon lowest-energy transition determined by the PCM/Response function calculation and the energy of the lowest-energy absorption band of the experimental UV–vis spectra of the smallest system investigated, that is, the H substituent. Note that in the present study we neglect the zero-point vibrational energy and we compare vertical excitation energy with the experimental absorption band maximum. Here, the following values were adopted as the CAM-B3LYP functional parameters: \( \alpha = 0.150, \beta = 0.03 \) and \( \delta = 0.97 \). The suitability of such values to the response function calculations addressing the other substituents was confirmed through the satisfactory reproduction of the excitation energy of the lowest-energy transitions (one or two) identified from the experimental UV–vis spectra.

One may point two plausible sources of discrepancies between the values adopted for the CAM-B3LYP functional parameters in the present study and the one by K. Okuno et al. The distinct class of compounds investigated is perhaps the main reason. However, another point that can contribute to such differences is that in the present study the values adopted for the CAM-B3LYP functional parameters were determined by performing linear response function calculations in combination with a PCM, while in the work conducted by K. Okuno et al. the values were determined based on the results of gas-phase calculations.

Finally, to confirm the donor-acceptor charge transfers involved on the main one- and two-photon absorption transitions of the substituents, the percentage contribution of the excitations to the transitions, and the KS molecular orbitals involved, were determined. The KS molecular orbitals were determined by DFT calculations using the tuned CAM-B3LYP/6-31 + G(d) approach in combination with IEF-PCM and using the Gaussian 2009 package.

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Author contributions
M.G.V. conceived the idea of this study and performed the nonlinear optical measurements while J.M. and M.B. synthesized the molecules and characterized their linear optical properties. D.L.S., R.Z., W.B. and H.A. performed the quantum chemical calculations. L.D.B., S.C., E.I. and C.R.M. supervised this study. All authors contributed to the writing of this manuscript.

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