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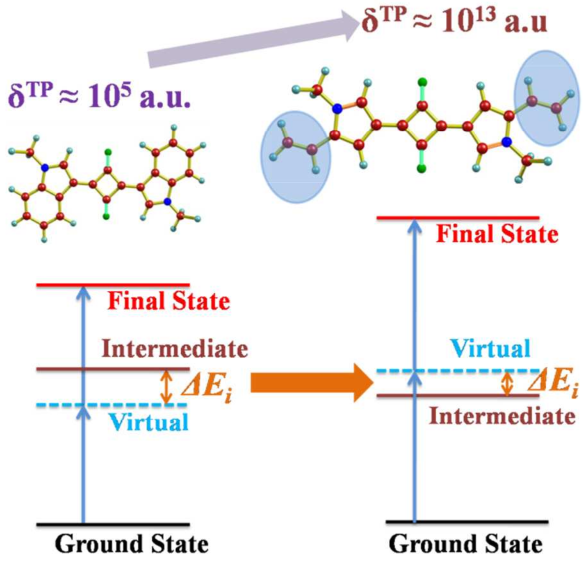
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ARTICLE TYPE

On the origin of very strong two-photon activity of squaraine dyes - A standard/damped response theory study

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In the present work, we are reporting the mechanism of very large increase in two-photon (TP) activity of squaraine based molecules upon changes of substituents. The replacement of a specific fused ring by ethylene or ethyne moieties enhances the TP transition strength of these molecules up to the order of 10^{13}au (~10^{10} GM), both in the gas phase as well as in dichloromethane solvent. Our calculations decisively establish that the reason for this large enhancement in TP activity of the studied systems is the severe decrease in the corresponding detuning energies. We explain this fact using the damped response theory calculations and provide a novel design strategy to control the detuning energy in such molecules. The results are benchmarked with the available experimental findings.

Introduction

Even 80 years since the first theoretical prediction[1] and more than 50 years after the first experimental verification,[2,3] two-photon absorption (TPA) is still a central theme for research in the field of non-linear optics. The quest for more and more two-photon (TP) active materials is triggered by the long list of applications in which they can be employed, in various advanced technological domains such as, among others,[4-6] 3D data storage,[7] photo-dynamic therapy[8] and optical limiting.[9,10] The inner mechanism and the computational aspect of the TPA process became more transparent and definitely more easily accessible after the development almost thirty years ago of modern analytical response theory (RT)[11-15] and, more recently, of time-dependent density functional theory (TDDFT).[16-18] Using the latter, one can easily calculate the TPA strength of large molecules.[19-21] Our groups have been quite active in the field; for recent work see for instance refs. 22 and 23. The TP strength δ^{TP} for a transition induced by a linearly polarized beam between the initial $|0\rangle$ and final $|f\rangle$ states is connected to the TP transition tensor S^{0f} through the quantity δ_{0f}^{TP}, given by the expression[21,24-27]

$$\delta_{0f}^{TP} = 2\sum_{\alpha,\beta} S_{\alpha\alpha}^{0f} S_{\beta\beta}^{0f} + 4\sum_{\alpha,\beta} S_{\alpha\beta}^{0f} S_{\alpha\beta}^{0f}\,. \qquad (1)$$

The relationship between δ_{0f}^{TP} and the TP transition strength, which in turn is directly related to experiment and is usually measured in GM, is discussed for example in Ref. 21, see also Supporting Information (SI).

Above $S_{\alpha\beta}^{0f}$ represents the TP transition tensor component and it depends on the transition dipole moments (TDMs) and on the corresponding excitation energies. In a sum-over-states formalism, for the degenerate case of two photons with equal circular frequency $S_{\alpha\beta}^{0f}$ can be written as[21,24-27]

$$S_{\alpha\beta}^{0f} = \sum_i \frac{\mu_\alpha^{0i}\mu_\beta^{if} + \mu_\beta^{0i}\mu_\alpha^{if}}{\Delta E_i^{(f)}} \qquad (2)$$

Here and above, $\alpha,\beta=\{x,y,z\}$, μ_α^{ij} is the α component of the TDM vector involving states $|i\rangle$ and $|j\rangle$ and $\Delta E_i^{(f)} = \hbar\left(\omega_{0i} - \omega_{0f}/2\right)$ is the detuning energy. In Figure 1 the latter is depicted for the specific case of a centrosymmetric molecule, for a TP transition between the ground XA_g and the first excited state of the same symmetry ($1A_g$), with a nearly resonant intermediate $1B_u$ state.

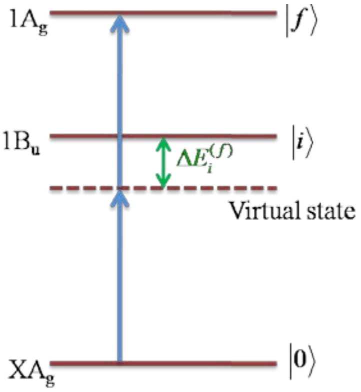

Fig. 1A schematic diagram showing three important states, their symmetry and detuning energy involved in TPA process in centro-symmetric molecules.

From Eq. (2) it is evident that the smaller the values of $\Delta E_i^{(f)}$, the larger will be $S_{\alpha\beta}^{0f}$ and as a consequence the larger will be δ_{0f}^{TP}. This suggests that, a careful control of the $\Delta E_i^{(f)}$ may lead to a sizeable increase in the TP activity. However, in the limits of double resonant TPA (RTPA), when $\Delta E_i^{(f)}$ becomes zero, we encounter a singularity problem in Eq. (2) and the standard approach to TPA, tailored to the case of single (ground and final states) resonance, fails. The results obtained using standard RT, for the nearly double resonant TPA processes, are in principle not reliable. Recently, damped response theory (DRT)[28,29] has been employed to develop a protocol for the calculation of TPA.[30] Since its development, DRT has proven to be an indispensable tool for studying several absorption and dichroism processes also in large molecules.[31-35] The DRT approach to TPA (DTPA from now on) has advantages with respect to the standard approach (STPA below) also beyond the cases of double resonance. With DTPA, the observable is determined directly, at a given frequency, resorting to a modified damped cubic response function. Therefore the TPA spectrum may be evaluated for selected frequency ranges, something which is especially convenient for large molecules with a high density of states, where STPA encounters problems, being targeted at individual excited states. Moreover, in the implementation of Ref. 30 an atomic-orbital based density matrix formulation, particularly suitable for studies on large systems, was used.

Herein we intend to propose a new design strategy for materials having large TP transition strengths, by controlling the detuning energy, $\Delta E_i^{(f)}$. To this end, we have considered the D-π-A-π-D structures (D = electron donor groups; A = electron poor 1,3-disubstituted C_4O_2 unit) of squaraine dyes, see Figure 2, which are well known for their large TP activity in combination with low energy, sharp and intense one photon (OP) absorption/emission bands in the visible to near infrared region.[36-45]

Computational Details

The ground state geometries of all these molecules, in gas phase and in CH_2Cl_2 solvent, were optimized at density functional level of theory using the B3LYP functional[46-48] and two sets of basis sets (a) 6-311G(d, p) for C, H and N atoms and (b) 6-311+G(d,p) for O atoms.[49,50] An extra diffuse function on the O-atoms was included to account for their excess negative charge. No constraint was applied during geometry optimization. Solvent phase geometry optimizations were carried out with the polarizable continuum model (PCM) of Tomasi et al.[51,52] Frequency calculations on the optimized geometries produced all real frequencies for these systems, which ensures that the geometries belong to minima on their respective potential energy surfaces. All the geometry optimizations and frequency calculations have been performed using Gaussian 09 suite of program.[53] In the next step, we have employed the linear and quadratic response theories within the framework of time-dependent density functional theory (TDDFT), as implemented in DALTON program package,[54,55] to compute the OP and TP absorption parameters of these molecules in both the gas phase as well as in CH_2Cl_2 solvent. The calculations were performed aiming at the lowest ten excited states for the molecules in C_{2h} symmetry, for the lowest five for the system in a C_2 arrangement. In this case also, PCM[51,52] was used for the solvent phase calculations. In the final stage of our study, we have employed the DTPA[30] implemented in LSDalton.[56] A damping factor Γ of 0.004 au (0.109 eV, intended as half width at half maximum, HWHM) was employed in the DTPA calculations. All the response theory calculations employed the CAMB3LYP functional[57-60] and aug-cc-pVDZ basis set.[61,62] CAMB3LYP has proven recently to be particularly suited for TPA studies involving in particular excited states of diffuse, charge transfer and Rydberg character.[63-67,22]

Results and Discussions

The ground state optimized structure of all the systems in gas phase are given in SI. The first four SQ1-based molecular structures (SQ1, SQ1-py, SQ1-C2H3 and SQ1-C2H) have a C_{2h} point group symmetry arrangement, whereas the last one, SQ2, belongs to the C_2 point group. It is important to mention that the SQ1 and SQ2 molecules are studied here since they can be seen as model systems for two experimentally studied molecules.[68,69] The first one[68] has n-Octyl groups replaced by $-CH_3$ groups in SQ1. The n-Hexyl groups present in the pyrrole rings of the squaraine studied in Ref. 69 are replaced by $–CH_3$ groups, and the $-NBu_2$ substituents by $-NMe_2$ groups, in SQ2, see Fig. 2. The replacements were made in order to reduce the computational cost.

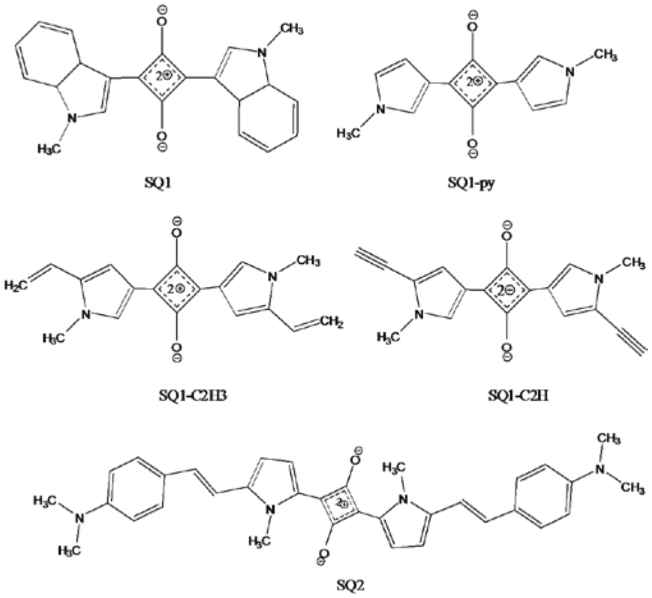

Fig. 2 The molecules considered in this work.

The OP absorption (OPA) data for the lowest active state of the five squaraine dyes of Fig. 2, both in gas phase and dissolved in CH_2Cl_2, are presented in Table 1 in the form of oscillator strengths, $f^{0i} = 2m_e\omega_{0i}\left|\mu^{0i}\right|^2 \big/ 3e^2\hbar$. The first OP active state of the SQ1-based molecules belongs to the B_u symmetry representation ($\left|i\right\rangle = \left|1\right\rangle = 1B_u$), whereas that of SQ2 can be labelled as a B state ($\left|i\right\rangle = \left|1\right\rangle = 1B$). From the results in Table 1 it is evident that the oscillator strength f^{01} for this state is largest (2.903 in gas phase and 3.286 in CH_2Cl_2) for SQ2, whereas it is the lowest (0.787 in gas phase and 1.092 in the solvated phase) for SQ1-py. This is mainly due to the difference in extent of π-conjugation between the two molecules. That the extent of π-conjugation is maximized in SQ2, and at its minimum in SQ1-py is somewhat expected, considering the structures shown in Fig. 1, and it is confirmed by the values of the ground to excited state transition dipole moment (μ^{01}), which, in gas phase, are 7.758 au for SQ2 and 3.390 au for SQ1-py, respectively. The corresponding values in CH_2Cl_2 are 8.708 au and 4.052 au, respectively. Indeed the strong correlation between extension of the π-conjugation and size of the transition dipole moment is evident throughout the series of molecules of Fig. 1, see Table 1. It is also important to note that, on moving from the gas to the CH_2Cl_2 solvent phase, in spite of a decrease in ω_{01} values, f^{01} for all the systems increases. We have noticed that it happens due to the large increase in the values of μ^{01} and the quadratic dependence of f^{0i} on μ^{0i}. The decrease in ω_{01} indicates that in these molecules the excited state is more stabilized by the moderately polar CH_2Cl_2 solvent than the ground state. This, in turn, increases the extent of charge transfer leading to an increase of μ^{01} and, therefore of the intensity of the OPA peaks for all the systems in solvent phase.

Table 1 Excitation energy ($\hbar\omega_{01}$), transition dipole moment (μ^{01}), oscillator strength (f^{01}) and orbital contributions for transition from the ground state ($|0\rangle$) to the lowest final OP active state ($|1\rangle$) of all the systems studied here in gas phase and solvated in CH_2Cl_2. Solvent phase data are given in bold-italics. H ≡ Highest Occupied Molecular Orbital (HOMO) and L ≡ Lowest Unoccupied Molecular Orbital (LUMO). The labels attached to H or L give the symmetry representation of the molecule these orbitals belong to (e.g. HB_g ≡ HOMO belonging to the B_g symmetry representation of the C_{2h} point group). The numbers in parenthesis give the amplitude (absolute value) of the dominant excitation in the TDDFT excitation vector.[66]

Systems	$\hbar\omega_{01}$ (eV)	μ^{01} (au)	f^{01}	Orbitals involved
SQ1	2.593 ***2.488***	4.039 ***4.654***	1.036 ***1.319***	HA_u-LB_g (0.70) ***HA_u-LB_g (0.70)***
SQ1-py	2.796 ***2.748***	3.390 ***4.052***	0.787 ***1.092***	HA_u-LB_g (0.70) ***HA_u-LB_g (0.71)***
SQ1-C2H3	2.707 ***2.621***	3.996 ***4.687***	1.059 ***1.406***	HA_u-LB_g (0.70) ***HA_u-LB_g (0.70)***
SQ1-C2H	2.712 ***2.641***	3.890 ***4.564***	1.006 ***1.346***	HA_u-LB_g (0.70) ***HA_u-LB_g (0.70)***
SQ2	2.001 ***1.792***	7.758 ***8.708***	2.903 ***3.286***	HA-LB (0.69) ***HA-LB (0.68)***

To get some a better insight into these $XA_g \rightarrow 1B_u$ (or XA → 1B) transitions, we have extracted information on the most important contribution to the excitation vector in the response calculation, following a procedure employed for example in Ref. 66. The results are listed in Table 1. It is apparent that for all the SQ1-based molecules the transitions have an HOMO (A_u) to LUMO (B_u) character, HOMO (A) to LUMO (B) for SQ2. The corresponding gas phase orbital pictures are shown in Fig. 3. Whereas for all the SQ1-based molecules the HOMOs and LUMOs are spread throughout the whole molecules, for SQ2, the LUMO is mainly localized in the central region while the HOMO electron density is again delocalized over the entire molecule. Therefore, in SQ1-based molecules the ground to excited state transition is predominantly local, whereas in SQ2 it involves a charge transfer from the long π-conjugated arms to the central region. In all these cases the lowest OP transition is primarily of π-π* character.

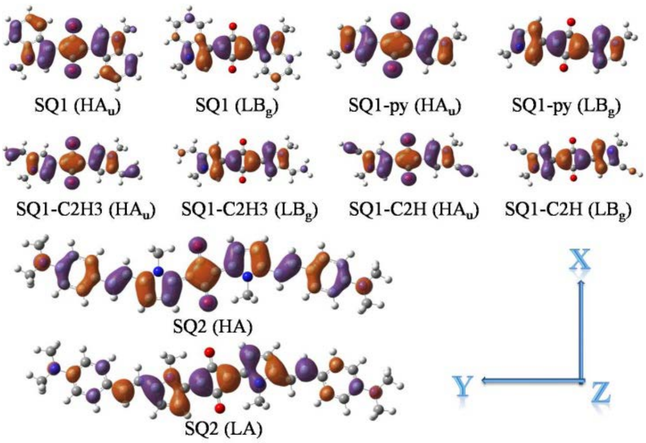

Fig. 3 Orbitals involved in the transition from ground to the lowest OP active state of the systems considered in this work.

The TP molecular parameter δ_{0f}^{TP} and detuning energies $\Delta E_i^{(f)}$ corresponding to the largest TP transition strengths for each of the systems studied here, computed both in gas phase and in CH_2Cl_2 solvent and obtained using STPA are collected in Table 2. Values of δ_{0f}^{TP} computed for all excited states considered in this study are supplied in SI. We note that the value of δ_{0f}^{TP} for SQ2 is larger than that for SQ1 in CH_2Cl_2, which is consistent with the experimental results for their analogue molecules. The reverse apparently holds for the gas phase.[68,69] The ratio of δ_{0f}^{TP} values for these two systems in gas phase is $9.50 \times 10^7 : 1.01 \times 10^7$ (≈9.4:1) whereas the same in a CH_2Cl_2 solution is $1.29 \times 10^7 : 4.67 \times 10^7$ (≈1:3.6). The corresponding experimental ratio[68,69] for analogue molecules in CH_2Cl_2 is 1:60. It is important to note that on moving from gas to solvent phase, the value of δ_{0f}^{TP} (summed over all allowed transitions considered, $\sum_f \delta_{0f}^{TP}(\omega_{0f})$) decreases by more than six times for SQ1, whereas it increases by a factor of about four for SQ2. Note also that the most intense TP active state for SQ2 changes from 5A (in gas phase, ΔE_{XA-5A} = 4.27 eV) to 2A (in CH_2Cl_2 solvent, ΔE_{XA-2A} = 3.43 eV) whereas it remains the same ($4A_g$, with a change in excitation energy from 5.11 eV to 5.12 eV) for SQ1. The opposite trend for the TPA of these two molecules may be correlated with the corresponding change in detuning energy on moving from gas to the solvated medium. Upon addition of substituents as the vinylinic or acetylenic groups to SQ1-py δ^{TP} increases instead to a large extent, especially when taking the effect of the solvent into account. This increase is related to the change in detuning energy $\Delta E_i^{(f)}$ upon substitution. The decrease of $\Delta E_i^{(f)}$ afforded by the solvent is much larger than that in gas phase particularly for the SQ1-C2H3 and SQ1-C2H molecules. Moving from gas phase to CH_2Cl_2, $\Delta E_i^{(f)}$ for SQ1-C2H3, changes from 0.050 eV to 0.004 eV, the same value reached for SQ1-C2H down from 0.028 eV. Such a small value of $\Delta E_i^{(f)}$ leads to a very large value for δ_{0f}^{TP} of these two systems, reaching as much as 1.15×10^{13} au for SQ1-C2H3 ($\delta^{TP} \approx 10^{10}$ GM).

Table 2 TPA molecular parameter δ_{0f}^{TP} (in au) and detuning energy, $\Delta E_i^{(f)}$ (in eV) corresponding to the largest TP transition strengths (among the lowest ten excited states of each TP allowed symmetry for SQ1 and its derivatives, the lowest five in both A and B symmetries for SQ2) for each of the systems studied here, both in gas phase and solvated in CH_2Cl_2. STPA results. The label of the final excited state considered for this analysis is also given. The intermediate nearly resonant state is in all cases the $1B_u$ state (1B for SQ2) state. See also Fig. 4 and full data in SI.

System	In gas phase			In CH_2Cl_2		
	Sym	$\Delta E_i^{(f)}$ (eV)	δ_{0f}^{TP} (au)	Sym	$\Delta E_i^{(f)}$ (eV)	δ_{0f}^{TP} (au)
SQ1	$4A_g$	0.038	9.50×10^7	$4A_g$	0.072	1.29×10^7
SQ1-py	$3A_g$	0.087	2.21×10^7	$3A_g$	0.064	2.91×10^8
SQ1-C2H3	$4A_g$	0.050	2.60×10^8	$3A_g$	0.004	1.15×10^{13}
SQ1-C2H	$3A_g$	0.028	1.26×10^9	$3A_g$	0.004	8.92×10^{11}
SQ2	5A	0.133	1.01×10^7	2A	0.079	4.67×10^7

As mentioned above, in cases where the conditions of double resonance are approached in a TPA process, the limitations of STPA make its analysis particularly critical. In case of molecules of large size, and in regions of the excitation spectrum where the density of excited states becomes notable, one way to circumvent the shortcomings of STPA can be found in DTPA, currently implemented for isolated molecules.[30] Out of the five molecules discussed in this paper, SQ1 and its derivatives were found to be manageable with current computational resources in our laboratories. In order to verify the predictions of gas-phase STPA, we have analyzed all these four SQ1-based molecules using DTPA. In DTPA, an empirical complex damping parameter $i\Gamma$ is introduced into the response function equations, thereby extending their realm to the entire range of frequencies, including the complex ones. The first formulation of damped response theory, not yet extended (to our knowledge) to the study of TPA, and where the empirical damping term is introduced in the standard Ehrenfest equation, was presented by Norman *et al.* in 2005.[28] An equivalent formulation was proposed more recently by Kristensen *et al.*[29] In Ref. 29 the authors introduced empirical excited states lifetimes directly into the cubic response functions, using therefore complex excitation energies. In Ref. 30 this approach to damped response theory was extended to the treatment of TPA. DTPA, unlike STPA, yields the whole absorption profile in the desired frequency range directly, without any reference to the individual states. Differences between STPA and DTPA arise in particular when the absorption TP wavelength approaches the excitation energy of the intermediate states. This case of double resonance (the first resonance corresponding to the conservation of energy condition in TPA, $2\omega \approx \omega_{0f}$, the second to the condition $\omega \approx \omega_{0i}$, which together amount therefore to $\Delta E_i^{(f)} \approx 0$) is problematic not only for theoretical calculations but also for experiment, as TPA and OPA spectra tend to overlap. In the present case, we have employed DTPA to calculate the gas-phase δ^{TP} of all the four SQ1-based molecules in a range of frequencies from 0.030 to 0.095 au with a step of 0.01 au. This range covers for all these four molecules the area of the spectrum approaching the double resonance condition, placed roughly between 2.7-2.8 eV (the range of excitation energies of the lowest excited - nearly resonant - B_u excited state, see SI). The DTPA spectra are shown in Fig. 4, where the DTPA results are shown together with the corresponding stick STPA data, identifying in red final states of A_g symmetry, in blue those of B_g symmetry. Final states of both symmetries with TP strengths weaker than needed to appear as sticks in the spectra are identified with dotted vertical lines with the appropriate colour code. The vertical dotted line in dark green indicates the position of the lowest OP active (B_u) state. The detuning energies discussed above are explicitly indicated. All four molecules display very large values for δ^{TP}, particularly strong in the 2.7-2.8 eV photon frequency range. The remarkable absorption is due to the particular TP efficiency of the total symmetric excited states lying in the region, and it is boosted by a near resonance with the first OP active state of B_u symmetry.

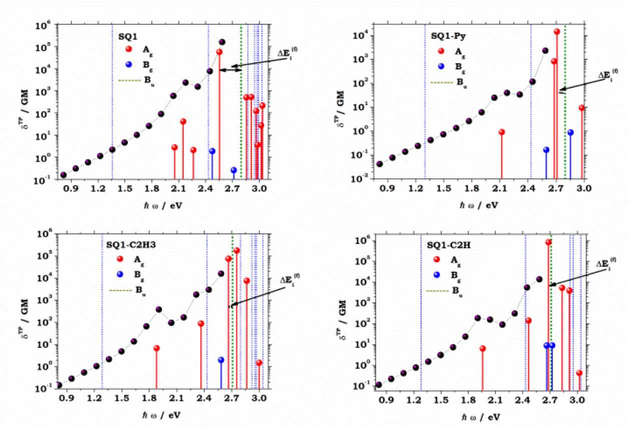

Fig. 4 Gas-phase TPA spectra of four out of the five molecules studies here. DTPA spectra ($\delta^{TP}(\omega)$, Eq. 4 in SI) reported together with the corresponding stick STPA results ($\delta^{TP}(\omega_{0f})$, cf. Eq. 1 in SI). For the latter, a colour code distinguishes A_g (red) and B_g (blue) TP active states. Dotted vertical lines indicate TP active states whose TP strength is not showing in the scale of the figure. The vertical dotted line in dark green shows the location of the lowest OP active (TP transparent) $1B_u$state. Note that the frequency in abscissa is that of the TP process, and therefore the sticks show at half the excitation energy of the final state, whereas the dark green dotted lines are at the excitation energy of the $1B_u$ state. That allows to display on each panel the detuning energy, defined here as $\left|\omega_{XA_g,nA_g}/2-\omega_{XA_g,1B_u}\right|$, where the final TP active state nA_g yields the most intense TP strength in the panel.

Conclusions

In the first systematic *ab initio* TPA study carried out within the framework of the rather recently developed damped response theory approach,[30] we have studied the TPA process in squaraine based D-π-A-π-D type of molecules, whose two photon activity can largely be improved by simple geometrical substitutions. Indeed our calculations clearly show that by removing the fused ring and placing the ethylene or ethyne moieties with symmetry point group unaltered, decreases the detuning energies ($\Delta E_i^{(f)}$) of these molecules to a great extent, which in turn causes an enormous rise in their TP activity. The use of a damped TPA approach proves to be of major relevance in order to validate our results and to avoid the breakdown of standard response theory in the double resonance conditions applying in the small $\Delta E_i^{(f)}$ limit. In short, the present study decisively establishes that it is possible to fine tune the $\Delta E_i^{(f)}$ values and hence the TP activity of squaraine based systems by simple chemical modification.

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Notes and references

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† Electronic Supplementary Information (ESI) available: (a) Gas and solvent phase optimized Cartesian coordinates of all systems; (b) excitation energies, excitation wavelengths, transition moments and STPA two-photon transition strengths for the lowest ten electronic states of each symmetry; (c) STPA two-photon tensor elements; (d) Full set of DTPA results. See DOI: 10.1039/b000000x/

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