

# Uncovering Structure–Property Relationships in Push–Pull Chromophores: A Promising Route to Large Hyperpolarizability and Two-Photon Absorption

Alessio Cesaretti, Paolo Foggi, Cosimo G. Fortuna, Fausto Elisei, Anna Spalletti, and Benedetta Carloti\*

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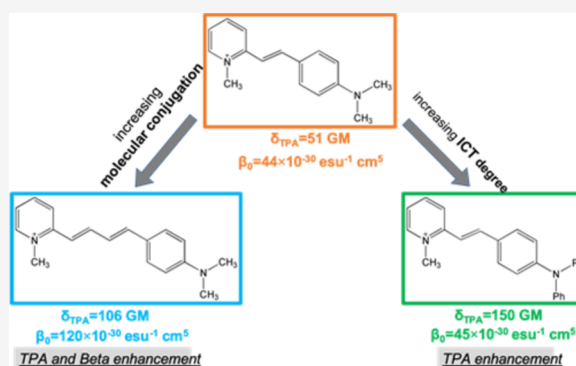
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**ABSTRACT:** In this investigation, we report the first hyperpolarizabilities and two-photon absorption cross sections of a large series of 12 push–pull cationic chromophores. All of these dyes show a dipolar acceptor<sup>+</sup>– $\pi$ –donor structure, where the nature of the donor and acceptor units and  $\pi$ -bridge was synthetically tuned to allow insightful comparisons among the molecules. The hyperpolarizability was obtained through a solvatochromic method, by exploiting the rare negative solvatochromism exhibited by the investigated compounds. The two-photon absorption cross sections were determined through two-photon excited fluorescence measurements by means of a tunable nanosecond laser system for sample excitation. The nonlinear optical properties were discussed relatively to the photoinduced intramolecular charge transfer occurring in these donor–acceptor systems, investigated by femtosecond transient absorption experiments. We found a strong increase in hyperpolarizability upon increasing the molecular conjugation. Unexpectedly, the hyperpolarizability is almost unaffected by an increase in donor/acceptor strength and intramolecular charge transfer degree. Differently, the two-photon absorption cross sections of these dyes are enhanced by an increase in both molecular conjugation and intramolecular charge transfer efficiency. Several recent literature works have reported at the same time scattered information about the hyperpolarizability and two-photon absorption of small organic molecules. Our investigation is, to the best of our knowledge, the first attempt to uncover detailed structure–property relationships for these two nonlinear optical properties. Our results represent a promising route to achieve large hyperpolarizability and two-photon absorption in push–pull dyes and may drive the design of new efficient nonlinear optical materials.



## INTRODUCTION

Nonlinear optical materials are among the smartest materials of the current age owing to their frequency-tuning ability of laser light interacting with them.<sup>1</sup> Development of nonlinear optical materials is an area of frontier research due to extensive applications in optoelectronics, photonics, and medicine. Emerging technologies such as imaging, photodynamic therapy, and sensing are in continuous search for new, highly performing, low-cost materials. There is an always increasing need for new materials, and the one drawback of the use of inorganic nonlinear optical crystals is that they are very expensive. Great efforts have recently been made to explore other nonlinear optical materials comprising nanostructures, polymers, and molecular dyes. Among these, organic molecules are of paramount interest due to their large nonlinear optical responses, together with low production cost and flexibility of design. Organic dyes have attracted interest due to their environmentally friendly nature, convenient purification, and synthesis. During the last years, chemists have paid deep attention to organic compounds bearing electron donor (D) and acceptor (A) groups linked by  $\pi$ -conjugated bridges owing

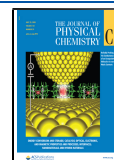
to their appealing nonlinear optical response. The nonlinear optical properties of D– $\pi$ –A compounds can be finely tuned by selecting appropriate D, A units and  $\pi$ -bridges at suitable positions. Such dipolar D– $\pi$ –A structures have recently shown very high hyperpolarizabilities<sup>2</sup> and large two-photon absorption.<sup>3</sup> In this respect, great interest has lately been devoted to cationic chromophores for their surprisingly high nonlinear optical responses<sup>4,5</sup> and also for their water solubility, which is really appealing in view of their possible use in biology and medicine.<sup>6–9</sup>

Several literature studies have reported at the same time results concerning different nonlinear optical properties such as two-photon absorption and first/second hyperpolarizabilities. However, most of these investigations are purely computa-

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tional and report predictions of these properties obtained by means of quantum simulations.<sup>10,11</sup> One of the few experimental works performed to measure two-photon absorption as well as second hyperpolarizability ( $\gamma$ ) by four-wave mixing spectroscopy deals with only one investigated organic dye.<sup>12</sup> Only more recently, several research works have reported both two-photon absorption and first hyperpolarizability ( $\beta$ ) obtained either computationally<sup>13,14</sup> or by a joint computational and experimental effort<sup>15,16</sup> in a series of organic systems. It is noteworthy that in all of these studies, the molecular dye exhibiting the largest two-photon absorption of the series never matched the one exhibiting the largest hyperpolarizability. However, these interesting results have not been discussed in terms of structural features possibly having different effects on the two distinct nonlinear optical properties. This is where our investigation seeks to shed new light upon. The aim of the present work is to uncover structure–property relationships concerning both the two-photon absorption cross sections and the first hyperpolarizabilities in a large series of 12 push–pull systems.

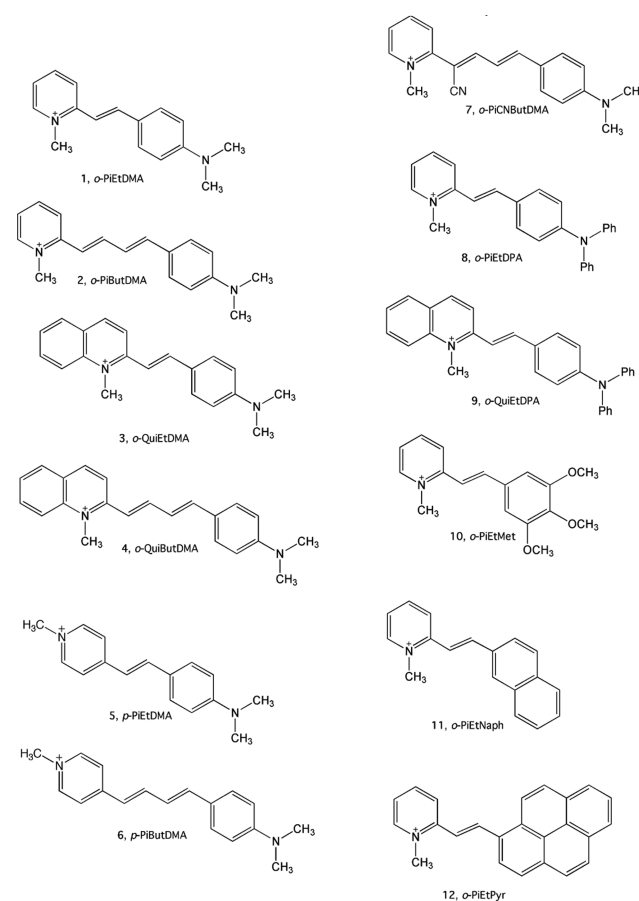
In particular, the chromophores under investigation are cationic  $A^+-\pi-D$  systems, where the electron-withdrawing moiety is a positively charged methyl pyridinium or methyl quinolinium. These cationic systems show a substantial water solubility and exhibit a rare negative solvatochromic behavior when investigated in different media.<sup>17–20</sup> In a previous paper,<sup>21</sup> we validated a new solvatochromic method for the evaluation of the hyperpolarizability of cationic push–pull compounds as derived from absorption and emission spectra recorded in solvents of different polarities.<sup>22,23</sup> Here, we apply this method to a large series of cationic dyes (Chart 1). For these dyes, two-photon excited fluorescence measurements were performed by employing a nanosecond tunable laser to experimentally measure their two-photon cross sections. In this series, not only the nature of the electron-accepting unit (methyl pyridinium, methyl quinolinium) but also the nature of the electron donor portion (dimethylamino phenyl, diphenylamino phenyl, trimethoxy phenyl, polycyclic aromatics) was changed. Additionally, the  $\pi$ -bridge in between the donor and acceptor was either ethylene or butadiene. In some cases, the position of attachment of the methyl pyridinium to the linker was also varied (*ortho* or *para*). The structural effects on the two nonlinear optical properties are discussed here in light of the photoinduced intramolecular charge transfer directly observed for these donor–acceptor systems by ultrafast spectroscopy through femtosecond transient absorption experiments.

## METHODS

**Chemicals.** The investigated compounds (1–12, shown in Chart 1) were synthesized following the previously reported procedures.<sup>17,24–30</sup> Measurements were performed in various solvents (Fluka, spectroscopic grade): chloroform ( $\text{CHCl}_3$ ), dichloromethane (DCM), 1,2-dichloroethane (DCE), acetone (Ac), dimethyl sulfoxide (DMSO), acetonitrile (MeCN), 2-propanol (PrOH), ethanol (EtOH), methanol (MeOH), water (W), and their mixtures.

**Experimental Techniques.** A PerkinElmer Lambda 800 spectrophotometer was used for the absorption measurements. The fluorescence spectra, corrected for the instrumental response, were measured by a FluoroMax-4P spectrofluorimeter by HORIBA Scientific operated by FluorEssence. Dilute solutions (absorbance < 0.1 at the excitation wavelength,  $\lambda_{\text{exc}}$ )

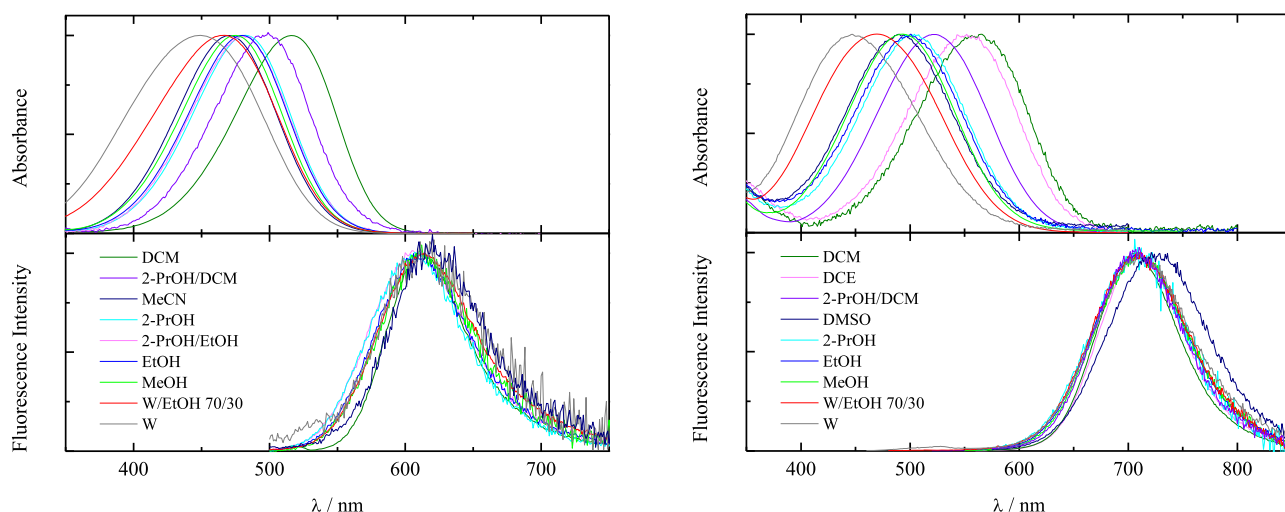
Chart 1. Molecular Structures of the Investigated Compounds



were used for fluorimetric measurements. The fluorescence quantum yield ( $\phi_F$ , uncertainty  $\pm 10\%$ ) was determined at  $\lambda_{\text{exc}}$  corresponding to the maximum of the first absorption band. Tetracene ( $\phi_F = 0.17$ <sup>31</sup> in aerated CH) was used as a fluorimetric standard.

The experimental setup for femtosecond transient absorption measurements has been widely described elsewhere.<sup>32–34</sup> In particular, the 400 nm excitation pulses of ca. 40 fs are generated by an amplified Ti:Sapphire laser system (Spectra Physics). The transient absorption setup (Helios, Ultrafast Systems) is characterized by a temporal resolution of ca. 150 fs and a spectral resolution of 1.5 nm. Probe pulses are produced in the 450–850 nm range by passing a small portion of 800 nm light through an optical delay line (with a time window of 3200 ps) and focusing it into a 2 mm thick Sapphire window to generate a white-light continuum. Ultrafast spectroscopic data were fitted by global and target analysis using the Surface Explorer and Glotaran softwares.<sup>35</sup>

Two-photon excited fluorescence measurements were performed using a Nd-YAG pump laser (Spectra Physics-Indi) at 355 nm and an optical parametric oscillator (OPO-Surelite P/N 996-0210, Continuum), which can be manually tuned to produce radiation between 410 and 2200 nm (signal between 410 and 750 nm; idler between 820 and 2200 nm). The fluorescence light is collected on a 1/4 meter monochromator equipped with a 1200 grooves/mm grating. Subsequently, there is a photomultiplier tube (Hamamatsu R3788), powered by a high-voltage power supply (PS-310, SRS), connected to an oscilloscope (LeCroy-Wave Runner-



**Figure 1.** Normalized absorption and emission spectra of **5** (left) and **6** (right) in solvents of different polarities.

LT322, 500 MHz, 200 MS/s, DSO) where the fluorescence intensity is read in mV. The two-photon absorption cross section was determined through the comparative method that uses a standard substance (a quadrupolar benzothiadiazole derivative in chloroform, compound **B** in ref 36) with a known cross section ( $\sigma = 125 \text{ GM at } 938 \text{ nm}$ ).

**Computational Details.** Quantum-mechanical calculations were carried out using the Gaussian 09 package.<sup>37</sup> Density functional theory (DFT) based on the CAM-B3LYP method was used to optimize the geometry and to obtain the properties of the substrates in the ground state, while the lowest excited singlet states were characterized by time-dependent (TD) DFT CAM-B3LYP excited-state calculations.<sup>38,39</sup> In both cases, a 6-31+G(d) basis set was employed. DCM solvation effects were included in the calculations by means of the conductor-like polarizable continuum model (CPCM).<sup>40</sup> Atomic charges and dipole moments were obtained using the quantum theory of atoms in molecules (QTAIM).<sup>41</sup> Calculations were carried out on the most stable conformation, that is, the *s-trans* conformation for all of the investigated compounds.

**Derivation of Hyperpolarizability.** The experimental results on the solvatochromism allowed information on the difference between the excited- and ground-state dipole moments ( $\mu_e - \mu_g$ ) to be obtained using eq 1, as derived on the basis of the Reichardt theory<sup>42,43</sup>

$$\Delta v = v_A - v_F = 11307.6 \frac{\Delta\mu^2 a_D^3}{\Delta\mu_D^2 a^3} E_T^N + \text{const} \quad (1)$$

where  $\Delta v = v_A - v_F$  is the Stokes shift (in  $\text{cm}^{-1}$ ),  $a$  is the cavity radius within Onsager's model (in cm), and  $E_T^N$  is an adimensional parameter accounting for solvent polarity. The  $a$  value was estimated as 60% of the calculated diameter along the CT direction (CT diameter) of the optimized structures. This procedure was chosen on the basis of the results reported in a previous paper<sup>44</sup> where  $a$  was calculated by integration of the solvent-accessible surface using both the Hartree–Fock and density functional theory optimized geometries and was found to be 60% of the CT diameter. The values  $\Delta\mu_D = 9 \text{ D}$  and  $a_D = 6.2 \text{ \AA}$  are relative to a reference compound (a betaine derivative).

From the slope resulting from the linear fitting of the graph reporting  $\Delta v$  as a function of  $E_T^N$ , the  $\Delta\mu$  value of the molecule (responsible for the observed solvatochromism) was derived. The hyperpolarizability was then calculated through the Oudar formula<sup>45</sup>

$$\beta_{CT} = \beta_{zzz} = \frac{3}{2h^2 c^2} \times \frac{v_{eg}^2 r_{eg}^2 \Delta\mu}{(v_{eg}^2 - v_L^2)(v_{eg}^2 - 4v_L^2)} \quad (2)$$

where  $r_{eg}$  is the transition dipole moment,  $v_{eg}$  is the transition frequency (in  $\text{cm}^{-1}$ , assumed to be the maximum of the bathochromic absorption band), and  $v_L$  is the frequency of the reference incident radiation (chosen as 1907 nm, for comparison purposes with experimental data) to which the  $\beta$  value would be referred. The  $r_{eg}$  value is related to the oscillator strength ( $f$ ) by  $r_{eg}^2 = \frac{3e^2 h}{8\pi^2 m c} \times \frac{f}{v_{eg}} = 2.13 \times 10^{-30} \times \frac{f}{v_{eg}}$  (with  $f$  being obtained from the absorption integrated band as  $f = 4.32 \times 10^{-9} \int \epsilon(v) dv$ ).<sup>46</sup>

The method based on the solvent effect on the spectra includes several approximations (with the evaluation of the cavity radius being the most critical one), thus allowing only a rough estimation of  $\beta$ , but it offers the advantages of simplicity and easy availability over the well-known method of electric-field-induced second-harmonic (EFISH) generation. The method here used gives the  $\beta_{CT}$  dominant contribution (corresponding to the  $\beta_{xxx}$  component of the  $\beta$  tensor when related to the CT transition). Moreover, being referred to the exciting laser frequency, the described method to calculate  $\beta_{CT}$  allows a direct comparison with the value measured by means of EFISH.

The static hyperpolarizability, whose value is instead frequency-independent, can be defined as follows<sup>47</sup>

$$\beta_0 = \frac{3}{2h^2 c^2} \times \frac{r_{eg}^2 \Delta\mu}{v_{eg}^2} \quad (3)$$

## RESULTS

**Negative Solvatochromism and Hyperpolarizability.** Figure 1 shows the solvent effect on the absorption and emission spectra of compounds **5** and **6**. Their spectral

Table 1. Spectral Properties of 5 and 6 in Solvents of Increasing  $E_T^N$  Parameter

solvent	$E_T^N$	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\Delta\nu/\text{cm}^{-1}$	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\Delta\nu/\text{cm}^{-1}$
		5			6		
DCM	0.321	517	614	3056	557	705	3770
DCE	0.346				552	710	4030
DCM/2-PrOH (50:50)	0.428	499	615	3780	523	705	4900
2-PrOH	0.552	481	607	4316	504	707	5700
EtOH/2-PrOH (50:50)	0.603	481	608	4343			
EtOH	0.654	480	611	4467	502	709	5820
MeOH	0.765	475	613	4739	492	712	6280
W/EtOH (50:50)	0.827				484	710	6580
W/EtOH (70:30)	0.896	467	612	5073	473	708	7020
W	1	448	617	6114	447	709	8270

Table 2. Calculated Parameters ( $\mu_g$ ,  $\mu_{e,\text{FC}}$ , and  $a$ ) for the Most Stable Rotamer of the Investigated Compounds and Experimental Parameters ( $\nu_{\text{eg}}$ ,  $f$ ,  $\beta_{\text{CT}}$ , and  $\beta_0$ ) Derived from Its Solvatochromism Using Equations 1, 2, and 3

comp. no.	$\mu_g/\text{D}$	$\mu_{e,\text{FC}}/\text{D}$	$a/10^{-8}\text{ cm}$	slope	$\Delta\mu_{\text{exp}}/\text{D}$	$\nu_{\text{eg}}/\text{cm}^{-1}$	$f$	$\beta_{\text{CT}}/10^{-30}\text{ esu}^{-1}\text{ cm}^5$	$\beta_0/10^{-30}\text{ esu}^{-1}\text{ cm}^5$
1	6.86 <sup>a</sup>	3.30 <sup>a</sup>	8.18	3270	-7.33	20 660	0.648	320	44
2	9.9 <sup>b</sup>	2.6 <sup>b</sup>	9.60	5260	-11.8	19 305	0.873	2930	120
3	1.6 <sup>b</sup>	9.4 <sup>b</sup>	9.57	1850	-6.98	18 050	0.847	1330	82
4	2.9 <sup>b</sup>	8.5 <sup>b</sup>	11.0	4650	-13.6	16 580	0.657	824	160
5	13.34	0.13	8.8	3770	-8.8	19 340	0.756	1770	75
6	17.85	1.29	10.1	5590	-13.2	17 953	1.068	2840	200
7	13.55	8.43	9.59	4180	-10.5	17 153	0.820	988	140
8	10.28 <sup>c</sup>	3.66 <sup>c</sup>	9.3	2301	-7.5	20 637	0.652	335	45
9	19.02	10.20	10.2	3450	-10.5	18 020	0.752	1710	110
10	14.62 <sup>a</sup>	4.94 <sup>a</sup>	8.15	3900	-7.97	25 640	0.605	58	23
11	15.0 <sup>d</sup>	4.50 <sup>d</sup>	8.19	3790	-8.0	26 667	0.618	48	21
12	18.26 <sup>a</sup>	4.55 <sup>a</sup>	8.60	2910	-7.46	21 650	0.531	159	32

<sup>a</sup>Calculated in DCM from ref 17. <sup>b</sup>Calculated in DCM from ref 19. <sup>c</sup>Calculated in DCM from ref 53. <sup>d</sup>Calculated in DCM from ref 20.

behavior is representative of the behavior generally exhibited by all of the compounds investigated here (see the Supporting Information and the references therein). Both the absorption and emission spectra are broad bands characterized by a bell-like shape. The absorption spectrum undergoes a significant shift toward shorter wavelengths, blue shift, when passing from a less polar solvent such as DCM to a highly polar solvent such as W (Table 1). The negative solvatochromism observed upon increasing the solvent polarity suggests that photoexcitation in these molecules takes place together with a decrease in the electronic-state dipole moment. The quantum chemical calculations indeed predicted a larger dipole moment for the ground state,  $\mu_g$ , relative to the excited state reached by light absorption, the Frank–Condon state,  $\mu_{e,\text{FC}}$  (see Tables 2 and S19). A negligible solvent effect has been generally revealed on the emission spectra. This result is consistent with a similar dipole moment for the relaxed emitting state and the ground state. Moreover, for several of the investigated molecules, experimental and computational evidences were previously reported uncovering the presence of two local emissive minima in the potential energy surface describing  $S_1$  leading to a dual emission behavior.<sup>18,48,49</sup> This behavior explains the fluoro-solvatochromism observed for compounds 3, 8, and 9 (see Figures S3, S5, and S13). A high dipole moment for the relaxed excited state, which discloses its intramolecular charge transfer character, has indeed been found in previous studies for several of the investigated molecules.<sup>17,19,48</sup> This finding is also in agreement with the large solvent effect on the fluorescence quantum yields of these molecules (see Supporting Information Tables S11–S13). The emission is strongly quenched in

the most polar solvents, where intramolecular charge transfer processes possibly accompanied by twisting of the molecular structure and consequent nonradiative deactivations to the ground state by internal conversion are favored.

It has to be noted that the absorption spectral shifts observed when passing from one molecule to another in this series could be well predicted using the simple Kuhn's model<sup>50</sup> (see the Supporting Information and, in particular, Table S14). This model considers the  $\pi$ -electrons of the chain between the pyridinium nitrogen and the dimethyl/phenyl amino group nitrogen for the investigated 1–9 dyes as electrons in a box as long as the chain length. In fact, different compounds with the same number of carbon atoms in the chain show very similar absorption energies (see, for instance, compounds 2 and 5, 1, and 8, 3, and 9) regardless of the structure.

A quantitative analysis of the spectral shifts as a function of solvent properties enables evaluation of the decrease in dipole moment occurring for these molecules upon photoexcitation ( $\Delta\mu_{\text{exp}}$ ) from the experimental data. Figure 2 reports the plots showing the linear increase of the Stokes shift with the solvent  $E_T^N$  parameter for the representative examples of compounds 5 and 6. The plots obtained for all of the investigated dyes are reported in the Supporting Information. From the slopes of the linear regressions of the experimental data, the  $\Delta\mu_{\text{exp}}$  values were obtained using the Reichard eq 1, and the results for molecules 1–12 are listed in Table 2. The  $\Delta\mu$  values are considered to be negative in agreement with the decrease in the dipole moment predicted to take place upon light absorption. For this reason, the frequency-dependent ( $\beta_{\text{CT}}$ ) and frequency-independent ( $\beta_0$ ) hyperpolarizabilities, eval-



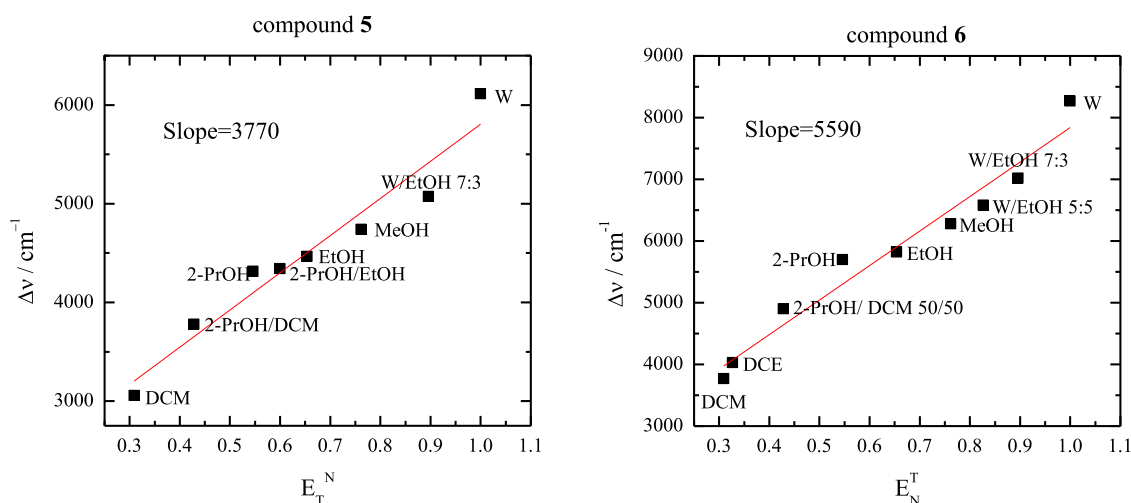


Figure 2. Plot of the Stokes shift as a function of  $E_T^N$  for 5 and 6.

uated through the Oudar eqs 2 and 3, respectively, are generally negative.<sup>21</sup> The absolute values of  $\beta_{CT}$  and  $\beta_0$  are reported in Table 2. The  $\beta_{CT}$  values have been computed by considering the frequency of the exciting laser (corresponding wavelength of 1907 nm) generally used in EFISH experiments.

The hyperpolarizability of these push–pull acceptor<sup>+</sup>– $\pi$ –donor systems is differently influenced by the nature of the electron acceptor portion, the electron donor group, and the  $\pi$ -bridge. The comparison among the frequency-independent  $\beta_0$  values (Table 2) allows for meaningful structure–property considerations for these cationic chromophores. A longer  $\pi$ -bridge (butadiene vs ethylene) implies a significantly enhanced hyperpolarizability (e.g.,  $\beta_0 = 44 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 1, *o*-PiEtDMA vs  $\beta_0 = 120 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 2, *o*-PiButDMA;  $\beta_0 = 82 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 3, *o*-QuiEtDMA vs  $\beta_0 = 160 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 4, *o*-QuiButDMA;  $\beta_0 = 75 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 5, *p*-PiEtDMA vs  $\beta_0 = 200 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 6, *p*-PiButDMA). Similar effects and comparable hyperpolarizabilities were obtained by EFISH measurements for *para*-substituted methyl pyridinium (acceptor unit) dibutylamino phenyl (donor unit) derivatives showing an ethylene or a butadiene  $\pi$ -bridge.<sup>51</sup> A more conjugated and larger electron acceptor moiety (quinolinium vs pyridinium) also has a positive impact on the hyperpolarizability (e.g.,  $\beta_0 = 44 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 1, *o*-PiEtDMA vs  $\beta_0 = 82 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 3, *o*-QuiEtDMA;  $\beta_0 = 120 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 2, *o*-PiButDMA vs  $\beta_0 = 160 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 4, *o*-QuiButDMA).<sup>51</sup> Additionally, it was found that a more conjugative position of attachment for the pyridinium electron acceptor portion (*para* vs *ortho*) causes an increase in the hyperpolarizability of these molecules (e.g.,  $\beta_0 = 44 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 1, *o*-PiEtDMA vs  $\beta_0 = 75 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 5, *p*-PiEtDMA;  $\beta_0 = 120 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 2, *o*-PiButDMA vs  $\beta_0 = 200 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 6, *p*-PiButDMA). All of these results unambiguously show a significant increase in the hyperpolarizability of these chromophores upon increasing their molecular conjugation. As clearly shown in Table 2, the  $\beta_0$  value indeed increases upon increasing the oscillator strength and upon red-shifting of the absorption spectrum.

On the other hand, other comparisons among the  $\beta_0$  values reported in Table 2 uncover the role played by the electron donor and electron acceptor units in affecting the hyper-

polarizability. When comparing two similar structures characterized by a different electron donor group (dimethylamino vs diphenylamino), the two  $\beta$  values are surprisingly found equal (e.g.,  $\beta_0 = 44 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 1, *o*-PiEtDMA vs  $\beta_0 = 45 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 8, *o*-PiEtDPA). Similarly, a change in the electron acceptor unit by adding a cyano group to the methyl pyridinium chromophore, which thus does not significantly affect the molecular conjugation, has only a little positive effect on the hyperpolarizability (e.g.,  $\beta_0 = 120 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 2, *o*-PiButDMA vs  $\beta_0 = 140 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 7, *o*-PiCNButDMA). These findings suggest that a change in the electron donor/electron acceptor group nature that does not affect the molecular conjugation (unchanged absorption spectrum) has a negligible/little impact on the hyperpolarizability of the investigated push–pull systems. This is consistent with literature reports showing that an increase in donor/acceptor group strength does not necessarily lead to an enhancement of the hyperpolarizability.<sup>52</sup>

When considering the 11 and 12 dyes, which do not bear a strong electron donor group but show an electron-rich extended aromatic moiety such as a naphthalene or a pyrene, lower hyperpolarizabilities were comparatively obtained. Once again, however, an increase in conjugation of the electron-rich unit (pyrene vs naphthalene) implies a slight enhancement of hyperpolarizability (e.g.,  $\beta_0 = 32 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 12, *o*-PiEtPyr vs  $\beta_0 = 21 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$  for 11, *o*-PiEtNaph).

**Femtosecond Transient Absorption.** The excited-state dynamics of these molecules after photoexcitation was investigated through femtosecond transient absorption experiments, which were carried out in solvents characterized by different polarities such as the less polar dichloromethane (DCM), the polar methanol (MeOH), and the highly polar water (W). The obtained results are reported in Figure 3 for the representative examples of compounds 5 and 6 in MeOH. The time-resolved absorption spectra are dominated in both cases by negative signals of stimulated emission above 550 nm. An excited-state absorption band, peaked around 550 nm for 5 and 600 nm for 6, respectively, is formed at early delays after excitation and subsequently decays. Below 520 nm, the tail of the ground-state absorption is clearly visible in the case of 5. For both dyes as well as for all of the other investigated systems (see Figure S23 for 7 and 9 in MeOH and refs 17–20), a large red shift in time of the stimulated emission

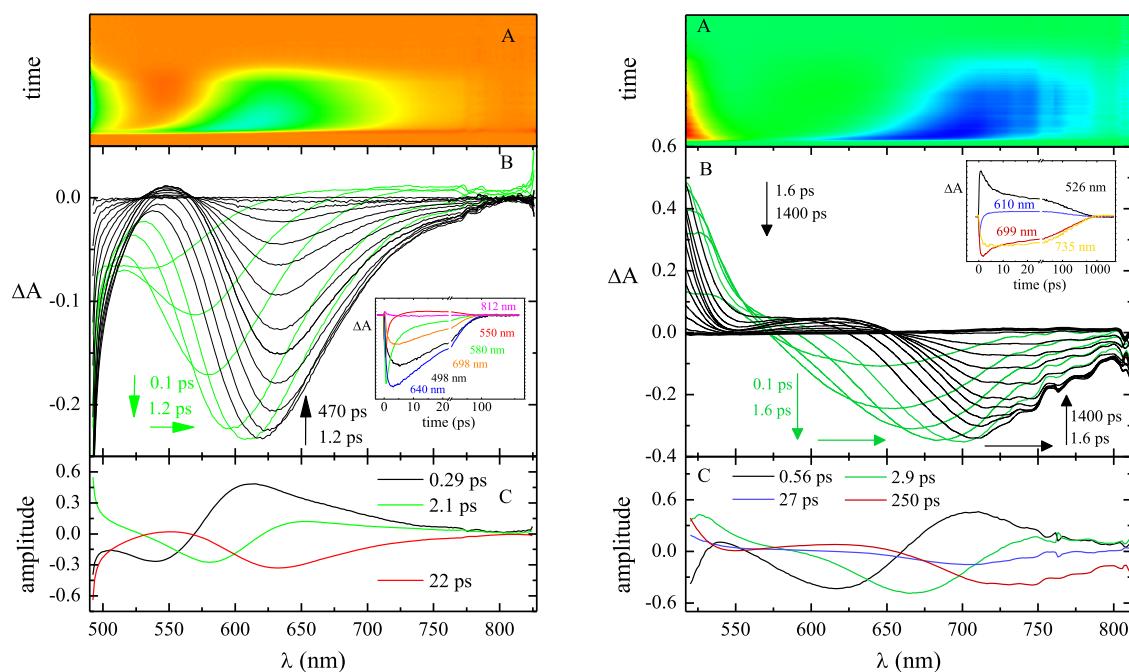


Figure 3. Femtosecond transient absorption data of compounds 5 (left) and 6 (right) in MeOH.

Table 3. Quenching Degree of the Intramolecular Charge Transfer Excited-State Lifetime Upon Increasing the Solvent Polarity as Estimated by the Femtosecond Transient Absorption Results

compound	1	2	3	4	5	6	7	8	9	10	11	12
quenching degree (DCM-MeOH) <sup>a</sup>	5.6	2.8	9.1	5	12	3.2	10	9.1	9.1	2.1	1	1.4
quenching degree (DCM-W) <sup>b</sup>	30	10	38	16	23	10	19	32		7.1		1.5
<sup>a</sup> $\tau_{\text{ICT,DCM}}/\tau_{\text{ICT,MeOH}}$ · <sup>b</sup> $\tau_{\text{ICT,DCM}}/\tau_{\text{ICT,W}}$												

band is observed during these measurements, which could be consistent with both relaxation processes and population dynamics to a lower energetic excited state. The global fitting of the acquired data revealed for 5 and 6 the presence of three and four exponential components, respectively (see Figure 3C and Table S15). The first two components of hundreds of femtoseconds and a few picoseconds perfectly match the well-known time constants for the inertial and diffusive solvation in MeOH. The last component characterized by lifetimes of 22 and 250 ps for 5 and 6, respectively, is assigned to the fully relaxed lowest excited singlet state, which shows an intramolecular charge transfer character— $S_1(\text{ICT})$ . The presence of two distinct emissive minima in the excited states of several molecules under investigation here—a low-dipole-moment intermediate locally excited state and a high-dipole-moment relaxed ICT state—has been observed in previous experimental and theoretical studies by our research group.<sup>17,19,48</sup> In the case of 6, an intermediate transient with a lifetime of 27 ps is indeed also found. This component can be associated with the low-dipole-moment excited state reached by light absorption— $S_1(\text{LE})$ . This  $S_1(\text{LE})$  state, which for 6 is observed as a separate component, shows instead a lifetime shorter than solvent relaxation in the case of 5.<sup>17</sup> The photoinduced intramolecular charge transfer is therefore fast, faster than solvation when the  $\pi$ -bridge is an ethylene, and slow, slower than solvation when the  $\pi$ -bridge is a butadiene. This result suggests that the effect of a longer  $\pi$ -bridge is to slow down the intramolecular charge transfer in these cationic molecules.

A convenient way to obtain an estimation of the excited-state intramolecular charge transfer degree of these molecules is to consider the solvent effect on their photophysics and excited-state dynamics. As it was already mentioned above, the observed quenching of the fluorescence quantum yields upon increasing the solvent polarity is caused by the enhancement in the twisted intramolecular charge transfer (TICT) character of the excited states of these dyes in the most polar solvents (see Tables S11–S13). The TICT nature of the lowest excited singlet state for these molecules has been proved by investigating the viscosity effect on its lifetime under isopolarity conditions (see the results of the femtosecond transient absorption measurements in MeOH/glycerol mixtures, two solvents characterized by a similar polarity, reported in Table S18). Moreover, previous studies from our group about compounds 1 and 10<sup>25</sup> have shown that a highly viscous medium, such as a hydrogel, is able to completely inhibit the formation of the final relaxed ICT state thus strongly confirming its TICT nature. In general, the excited-state deactivation investigated by ultrafast transient absorption becomes faster upon increasing the solvent polarity. In particular, the lifetime of the relaxed intramolecular charge transfer state— $S_1(\text{ICT})$ —is significantly shortened when passing from the less polar solvent DCM to the polar MeOH and W (see Tables S15–S17). The amount of quenching of this lifetime ( $\tau_{\text{ICT}}$ ) with the solvent polarity can be quantified according to simple equations ( $\tau_{\text{ICT,DCM}}/\tau_{\text{ICT,MeOH}}$  or  $\tau_{\text{ICT,DCM}}/\tau_{\text{ICT,W}}$ ) and can be considered an indication of the excited-state ICT degree for these molecules (Table 3).

The large series of molecules here investigated provide a basis for insightful comparisons and considerations about structure–property relationships as related to their photo-induced ICT degree (Table 3). First of all, looking at Table S15, it is apparent that a stronger degree of quenching is obtained when considering an ethylene (5.6 and 12 when passing from DCM to MeOH for **1**, *o*-PiEtDMA and **5**, *p*-PiEtDMA, respectively) with respect to a butadiene  $\pi$ -linker (2.8 and 3.2 for **2**, *o*-PiButDMA and **6**, *p*-PiButDMA, respectively). A longer  $\pi$ -bridge has a significantly negative effect on the intramolecular charge transfer efficiency in these molecules. A second important observation can be deduced by looking at Table S16. A quenching of 5.6 times is observed when passing from DCM to MeOH for **1**, *o*-PiEtDMA. When replacing the pyridinium electron acceptor moiety with a quinolinium (**3**, *o*-QuiEtDMA) or when replacing the dimethylamino donor group with a diphenylamino (**8**, *o*-PiEtDPA) or both (**9**, *o*-QuiEtDPA), a same quenching degree of 9.1 is found. This result demonstrates that the ICT efficiency is enhanced by employing a stronger electron donor group (diphenylamino vs demethylamino) or electron acceptor unit (quinolinium vs pyridinium), but the effect is not additive. A third point can be deduced by looking at Table S17. Once again, when considering a stronger electron acceptor by adding a cyano group to the pyridinium unit, a stronger degree of quenching and therefore a more efficient ICT is observed (2.8 and 10 upon passing from DCM to MeOH for **2**, *o*-PiButDMA and **7**, *o*-PiCNButDMA, respectively). Our ultrafast spectroscopic results clearly suggest that an increase in molecular conjugation or in the electron donor/acceptor strength brings about opposite effects, with the former having a negative impact on the ICT efficiency, whereas the latter exerts a positive influence.

**Two-Photon Absorption.** In the large group of the investigated dyes, several molecules were found to be poorly fluorescent because of the very important intramolecular charge transfer taking place during their excited-state deactivation. However, for some of the investigated compounds (e.g., **1**, **2**, **3**, **5**, **6**, **7**, and **8**), a significant fluorescence quantum yield of 1–30% was measured, at least in less polar solvents such as DCM (see Tables S11–S13). For these fluorophores, two-photon excited fluorescence measurements were carried out by employing a tunable nanosecond laser system for excitation in the infrared spectral range. For this reason, the two-photon absorption cross sections ( $\delta_{\text{TPA}}$ ), obtained here by the comparative method, are reported in Table 4, as evaluated at an excitation wavelength roughly corresponding to the double of the corresponding linear absorption maximum.

The obtained results demonstrate the important effect of both the molecular conjugation and the ICT degree on this nonlinear optical property. The two-photon cross section is doubled when an ethylene spacer ( $\delta_{\text{TPA}} = 51$  GM for **1**, *o*-PiEtDMA) is replaced with a butadiene spacer ( $\delta_{\text{TPA}} = 106$  GM for **2**, *o*-PiButDMA). Also, the two-photon cross section is enhanced by almost a factor of 5 when the position of attachment of the pyridinium acceptor unit is changed from *ortho* ( $\delta_{\text{TPA}} = 51$  GM for **1**, *o*-PiEtDMA) to *para* ( $\delta_{\text{TPA}} = 230$  GM for **5**, *p*-PiEtDMA). These findings show the strong positive impact of an increase in molecular conjugation on the two-photon absorption response. At the same time, a significant increase (by three times) in two-photon absorption is observed when replacing the dimethylamino donor ( $\delta_{\text{TPA}} =$

**Table 4.** Two-Photon Absorption Cross Sections of the Investigated Compounds in DCM at the Excitation Wavelength Roughly Corresponding to the Double of Their Linear Absorption Maxima

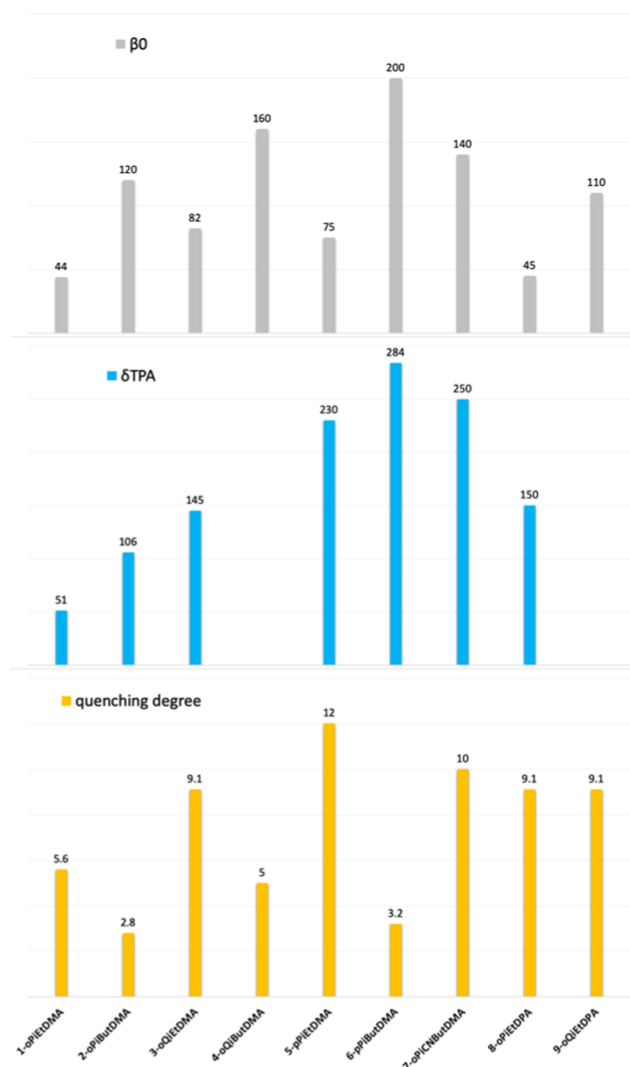
compound	$\delta_{\text{TPA}}/\text{GM}$ ( $\lambda_{\text{TPA}}/\text{nm}$ )
<b>1</b>	51 (985)
<b>2</b>	106 (1095)
<b>3</b>	145 (1120)
<b>5</b>	230 (1000)
<b>6</b>	284 (1120)
<b>7</b>	250 (1120)
<b>8</b>	150 (1025)

51 GM for **1**, *o*-PiEtDMA) with a diphenylamino group ( $\delta_{\text{TPA}} = 150$  GM for **8**, *o*-PiEtDPA) or when replacing the pyridium acceptor ( $\delta_{\text{TPA}} = 51$  GM for **1**, *o*-PiEtDMA) with a quinolinium ( $\delta_{\text{TPA}} = 145$  GM for **3**, *o*-QuiEtDMA). Also, the two-photon cross section is more than doubled by adding a cyano group ( $\delta_{\text{TPA}} = 250$  GM for **7**, *o*-PiCNButDMA) to the electron-deficient pyridium moiety ( $\delta_{\text{TPA}} = 106$  GM for **2**, *o*-PiButDMA). These findings show the positive impact of a stronger electron donor/acceptor couple and enhanced ICT degree on this nonlinear optical property.

## DISCUSSION

In this investigation, steady-state and time-resolved spectroscopy, with both nanosecond and femtosecond time resolutions, has been employed to obtain information about the nonlinear optical (NLO) properties (hyperpolarizability and two-photon absorption) of a large series of structurally analogous push–pull dipolar cationic chromophores (acceptor<sup>+</sup>– $\pi$ –donor). Our findings are summarized in Figure 4. In the figure, the frequency-independent hyperpolarizability ( $\beta_0$ ) as evaluated by the solvatochromic method and the two-photon absorption cross section ( $\delta_{\text{TPA}}$ ) as obtained by two-photon excited fluorescence measurements are reported, together with the excited-state intramolecular charge transfer degree (quenching degree) as estimated from the ultrafast spectroscopic results. It is well known that the intramolecular charge transfer (ICT) has an important effect on the nonlinear optical properties of organic molecules.<sup>23,28</sup> However, here, we have used spectroscopic experiments with femtosecond time resolution to quantify the ICT degree of the investigated push–pull systems and correlate it with their NLO response.

We found that both the molecular conjugation and the intramolecular charge transfer character of the excited states strongly influence the nonlinear optical response. However, the two considered nonlinear optical properties (hyperpolarizability and two-photon absorption cross section) are differently affected by these molecular features. The hyperpolarizability is highly influenced by the system conjugation, but it is surprisingly almost unaffected by the excited-state intramolecular charge transfer degree as evaluated from the ultrafast dynamics. Differently, the two-photon absorption cross sections are strongly enhanced by both a conjugation and an intramolecular charge transfer degree increase. Whether the excited-state intramolecular charge transfer degree of these chromophores increases or decreases, the hyperpolarizability and two-photon absorption cross section show an increase upon increasing the molecular conjugation. On the other hand, if the system conjugation is not changed, the effect of the intramolecular charge transfer degree is extremely important



**Figure 4.** Static hyperpolarizability ( $\beta_0$  in  $10^{-30} \text{ esu}^{-1} \text{ cm}^5$ ), two-photon absorption cross section ( $\delta_{\text{TPA}}$  in GM), and quenching degree upon increasing solvent polarity ( $\tau_{\text{ICT,DCM}}/\tau_{\text{ICT,MeOH}}$ ) for the investigated compounds.

on the two-photon absorption but practically negligible on the hyperpolarizability.

## CONCLUSIONS

This study represents a successful attempt to uncover the structure–property relationships for two nonlinear optical properties (first hyperpolarizability and two-photon absorption cross section) in a large series of push–pull cationic chromophores. In these dipolar acceptor<sup>+</sup>– $\pi$ –donor dyes, the nature of the donor and acceptor units and that of the  $\pi$ -linker were synthetically tuned, allowing important comparisons among the molecules to be drawn. We found a strong increase in hyperpolarizability upon increasing the molecular conjugation, whereas the hyperpolarizability is almost unaffected by an increase in the donor/acceptor strength. Differently, an enhancement in the two-photon absorption cross sections is observed in these dyes upon increasing both their conjugation and intramolecular charge transfer degree. Our investigation thus reports a large group of new, interesting, and low-cost organic materials for applications in nonlinear optics showing significant responses. Most importantly, our

results offer accurate guidelines regarding the crucial structural features to be considered when designing organic systems with large hyperpolarizability or two-photon absorption cross section.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c03536>.

Absorption and emission spectra for all of the investigated compounds in different solvents as well as plots of the Stokes shifts vs  $E_T^N$ ; fluorescence quantum yields; femtosecond transient absorption results; and computational results (PDF)

## AUTHOR INFORMATION

### Corresponding Author

**Benedetta Carlotti** – Department of Chemistry Biology and Biotechnology and Center of Excellence on Innovative Nanostructured Materials (CEMIN), University of Perugia, 06123 Perugia, Italy; [orcid.org/0000-0002-2980-2598](https://orcid.org/0000-0002-2980-2598); Email: [benedetta.carlotti@unipg.it](mailto:benedetta.carlotti@unipg.it)

### Authors

**Alessio Cesaretti** – Department of Chemistry Biology and Biotechnology and Center of Excellence on Innovative Nanostructured Materials (CEMIN), University of Perugia, 06123 Perugia, Italy

**Paolo Foggi** – Department of Chemistry Biology and Biotechnology and Center of Excellence on Innovative Nanostructured Materials (CEMIN), University of Perugia, 06123 Perugia, Italy; LENS (European Laboratory for Non-Linear Spectroscopy), 50019 Firenze, Italy; INO-CNR, Istituto Nazionale di Ottica—Consiglio Nazionale delle Ricerche, 50125 Firenze, Italy

**Cosimo G. Fortuna** – Department of Chemical Sciences, University of Catania, 95125 Catania, Italy

**Fausto Elisei** – Department of Chemistry Biology and Biotechnology and Center of Excellence on Innovative Nanostructured Materials (CEMIN), University of Perugia, 06123 Perugia, Italy

**Anna Spalletti** – Department of Chemistry Biology and Biotechnology and Center of Excellence on Innovative Nanostructured Materials (CEMIN), University of Perugia, 06123 Perugia, Italy

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c03536>

### Author Contributions

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### Notes

The authors declare no competing financial interest.

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