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Uncovering Structure-Property Relationships in Push-Pull Chromophores: a Promising Route to Large Hyperpolarizability and Two-Photon Absorption.

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

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3 KEYWORDS. Hyperpolarizability; Two-Photon Absorption; Push-Pull Chromophores;
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5 Nanosecond and Femtosecond Laser Spectroscopy; Solvatochromism.
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9 ABSTRACT. In this investigation, we report the first hyperpolarizabilities and two-photon
10 absorption cross sections of a large series of twelve push-pull cationic chromophores. All these
11 dyes show a dipolar Acceptor⁺- π -Donor structure, where the nature of the donor and acceptor
12 units and π -bridge were synthetically tuned allowing insightful comparisons among the molecules.
13
14 The hyperpolarizability was obtained through a solvatochromic method, by exploiting the rare
15 negative solvatochromism exhibited by the investigated compounds. The two-photon absorption
16 cross sections were determined through two-photon excited fluorescence measurements by means
17 of a tunable nanosecond laser system for sample excitation. The non-linear optical properties were
18 discussed relatively to the photoinduced intramolecular charge transfer occurring in these
19 donor-acceptor systems, investigated by femtosecond transient absorption experiments. We found
20 a strong increase in hyperpolarizability upon increasing the molecular conjugation. Unexpectedly,
21 the hyperpolarizability is almost unaffected by an increase in donor/acceptor strength and
22 intramolecular charge transfer degree. Differently, the two-photon absorption cross sections of
23 these dyes are enhanced by both an increase in molecular conjugation and intramolecular charge
24 transfer efficiency. Several recent literature works have reported at the same time scattered
25 information about the hyperpolarizability and two-photon absorption of small organic molecules.
26
27 Our investigation is to the best of our knowledge the first attempt to uncover detailed
28 structure-property relationships for these two non-linear optical properties. Our results represent
29 a promising route to achieve large hyperpolarizability and two-photon absorption in push-pull
30 dyes, and may drive the design of new efficient non-linear optical materials.
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Introduction

Non-linear optical materials are among the smartest materials of current age owing to their frequency tuning ability of laser light interacting with them.^[1] Development of non-linear 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 non-linear optical crystals is that they are really expensive. Great efforts have recently been made to explore other non-linear optical materials comprising nanostructures, polymers and molecular dyes. Among these, organic molecules are of paramount interest due to their large non-linear 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 π -conjugated bridges owing to their appealing non-linear optical response. The non-linear optical properties of D- π -A compounds can be finely tuned by selecting appropriate D, A units and π -bridges at suitable positions. Such dipolar D- π -A structures have recently shown giant hyperpolarizabilities^[2] and large two photon absorption.^[3] In this respect, great interest has lately been devoted to cationic chromophores for their surprisingly high non-linear optical responses^[4,5] but also for their water solubility which is really appealing in view of their possible use in biology and medicine.^[6-9]

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

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3 predictions of these properties obtained by means of quantum simulations.^[10,11] One of the few
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5 experimental works performed to measure two-photon absorption as well as second
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7 hyperpolarizability (γ) by four wave mixing spectroscopy deals with only one investigated
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9 organic dye.^[12] Only more recently, several research works have reported both two-photon
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11 absorption and first hyperpolarizability (β) either obtained computationally^[13,14] or by a joint
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13 computational and experimental effort^[15,16] in a series of organic systems. It is noteworthy that in
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15 all these studies the molecular dye exhibiting the largest two photon absorption of the series
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17 never matched the one exhibiting the largest hyperpolarizability. However, these interesting
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19 results have not been discussed in terms of structural features possibly having different effects on
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21 the two distinct non-linear optical properties. This is where our investigation seeks to shed new
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23 light upon. The aim of the present work is to uncover structure-property relationships
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25 concerning both the two-photon absorption cross sections and the first hyperpolarizabilities in a
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27 large series of twelve push pull systems.

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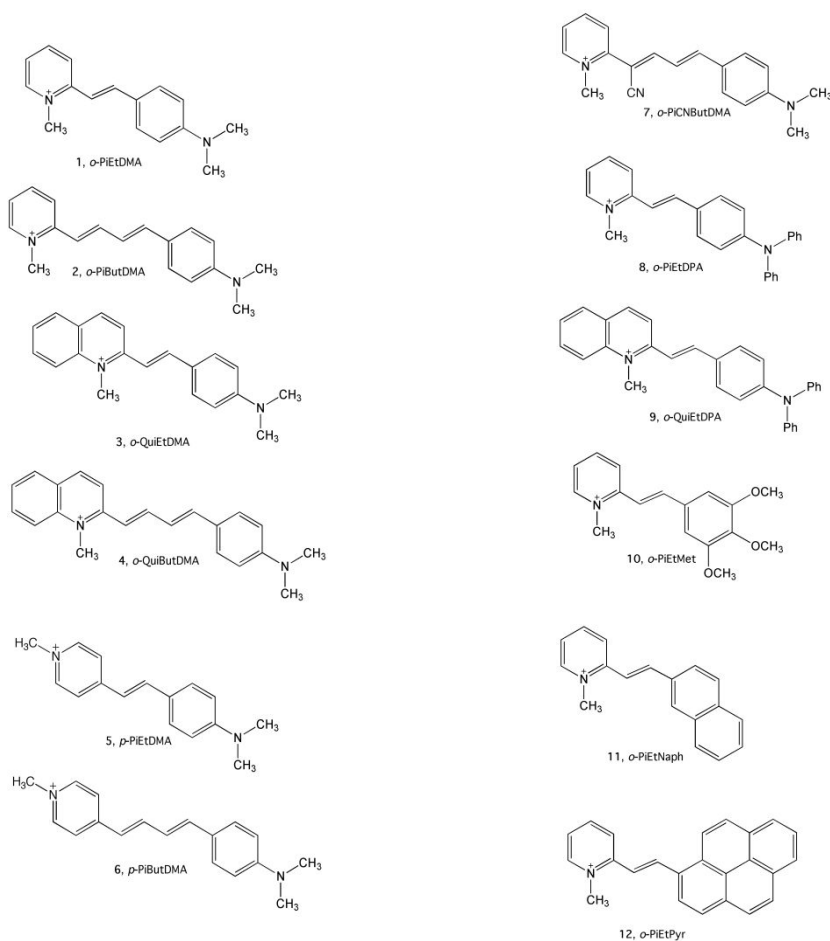


Chart 1. Molecular structures of the investigated compounds.

Methods

Chemicals. The investigated compounds (**1–12**, shown in Chart 1) were synthesized following previously reported procedures.^[17, 24–30] Measurements were performed in various solvents (Fluka, spectroscopic grade): chloroform (CHCl₃), dichloromethane (DCM), 1,2-dichloroethane (DCE), acetone (Ac), dimethyl sulphoxide (DMSO), acetonitrile (MeCN), 2-propanol (PrOH), ethanol (EtOH), methanol (MeOH), water (W) and their mixtures.

Experimental techniques. A Perkin–Elmer 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, λ_{exc}) were used for fluorimetric measurements. The fluorescence quantum yield (ϕ_{F} , uncertainty $\pm 10\%$) was determined at λ_{exc} corresponding to the maximum of the first absorption band. Tetracene ($\phi_{\text{F}} = 0.17$ ^[31] in aerated CH) was used as fluorimetric standard.

The experimental setup for femtosecond transient absorption measurements has been widely described elsewhere.^[32–34] 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 set up (Helios, Ultrafast Systems) is characterized by temporal resolution of ca. 150 fs and 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.^[35]

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3 Two-photon excited fluorescence measurements were performed using a Nd-YAG pump
4 laser (Spectra Physics-Indi) at 355 nm and an Optical Parametric Oscillator (OPO-Surelite P/N
5 996-0210, Continuum) which can be manually tuned to produce radiation between 410 and 2200
6 nm (signal between 410 and 750 nm; idler between 820 and 2200 nm). The fluorescence light is
7 collected on a ¼ meter monochromator equipped with a 1200 grooves/mm grating. Subsequently
8 there is a photomultiplier tube (Hamamatsu R3788), powered by a high voltage power supply
9 (PS-310, SRS), connected to an oscilloscope (LeCroy-Wave Runner-LT322, 500 MHz, 200
10 MS/s, DSO) where the fluorescence intensity is read in mV. The two-photon absorption cross
11 section was determined through the comparative method, that uses a standard substance (a
12 quadrupolar benzothiadiazole derivatives in chloroform, compound **B** in ref. 36) with a known
13 cross section ($\sigma=125$ GM at 938 nm).
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29 **Computational details.** Quantum-mechanical calculations were carried out using the
30 Gaussian 09 package.^[37] Density functional theory (DFT) based on the CAM-B3LYP method
31 was used to optimize the geometry and to obtain the properties of the substrates in the ground
32 state while the lowest excited singlet states were characterized by time dependent (TD) DFT
33 CAM-B3LYP excited-state calculations.^[38,39] In both cases a 6-31+G(d) basis set was
34 employed. DCM solvation effects were included in the calculations by means of the
35 Conductor-like Polarizable Continuum Model (CPCM).^[40] Atomic charges and dipole moments
36 were obtained by use of the quantum theory of atoms in molecules (QTAIM).^[41] Calculations
37 were carried out on the most stable conformation, that is the *s-trans* conformation for all of the
38 investigated compounds.
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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 by using eq. 1, as derived on the basis of Reichardt theory:^[42,43]

$$\Delta\nu = \nu_A - \nu_F = 11307.6 \frac{\Delta\mu^2 a_D^3}{\Delta\mu_D^2 a^3} E_T^N + const \quad (1)$$

where $\Delta\nu = \nu_A - \nu_F$ is the Stokes shift (in cm^{-1}), a is the cavity radius within Onsager's model (in cm), 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^[44] 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 $\Delta\mu_D = 9$ D and $a_D = 6.2$ Å are relative to a reference compound (a betaine derivative).

From the slope resulting from the linear fitting of the graph reporting the $\Delta\nu$ as a function of the E_T^N parameter, the $\Delta\mu$ of the molecule (responsible for the observed solvatochromism) was derived. The hyperpolarizability was then calculated through the Oudar formula:^[45]

$$\beta_{CT} = \beta_{zz} = \frac{3}{2h^2 c^2} \times \frac{\nu_{eg}^2 r_{eg}^2 \Delta\mu}{(\nu_{eg}^2 - \nu_L^2)(\nu_{eg}^2 - 4\nu_L^2)} \quad (2)$$

where r_{eg} is the transition dipole moment, ν_{eg} is the transition frequency (in cm^{-1} , assumed to be the maximum of the bathochromic absorption band) and ν_L is the frequency of the reference incident radiation (chosen as 1907 nm, for comparison purposes with experimental data) to which the β value would be referred. The r_{eg} value is related to the oscillator strength (f) by

$$r_{eg}^2 = \frac{3e^2h}{8\pi^2mc} \times \frac{f}{\nu_{eg}} = 2.13 \times 10^{-30} \times \frac{f}{\nu_{eg}} \quad (\text{with } f \text{ being obtained from the absorption integrated band as } f = 4.32 \times 10^{-9} \int \epsilon(\nu) d\nu).^{[46]}$$

The method based on the solvent effect on the spectra contains several approximations (with the evaluation of the cavity radius being the most critical one), thus allowing only a rough estimation of β , but it offers the advantage of simplicity and easy availability over the well-known method of electric-field-induced second-harmonic (EFISH) generation. The method here used gives the β_{CT} dominant contribution (corresponding to the β_{xxx} component of the β tensor when related to the CT transition). Moreover, being referred to the exciting laser frequency, the described method to calculate β_{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:^[47]

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

Results

Negative solvatochromism and hyperpolarizability

Figure 1 shows the solvent effect on the absorption and emission spectra of compounds **5** and **6**. Their spectral behavior is representative of the behavior generally exhibited by all the compounds here investigated (see the Supporting Information and references therein). Both the absorption and the emission spectra are broad bands characterized by a bell-like shape. The

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3 absorption spectrum undergoes a significant shift toward shorter wavelengths, blue shift, when
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5 passing from a low polar solvent such as DCM to an highly polar solvent such as W. The
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7 negative solvatochromism observed upon increasing the solvent polarity suggests that
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9 photoexcitation in these molecules takes place together with a decrease in the electronic state
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11 dipole moment. The quantum chemical calculations indeed predicted a larger dipole moment for
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13 the ground state, μ_g , relative to the excited state reached by light absorption, the Frank-Condon
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15 state, $\mu_{e,FC}$ (see Table 2 and Table S19). A negligible solvent effect has been generally revealed
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17 on the emission spectra. This result is consistent with a similar dipole moment for the relaxed
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19 emitting state and the ground state. Moreover, for several of the investigated molecules
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21 experimental and computational evidences were previously reported uncovering the presence of
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23 two local emissive minima in the potential energy surface describing S_1 leading to a dual
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25 emission behavior.^[18,48,49] This behavior explains the fluorosolvatochromism observed for
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27 compounds **3**, **8** and **9** (see Figures S3, S13 and S5). A high dipole moment for the relaxed
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29 excited state, which discloses its intramolecular charge transfer character, has indeed been found
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31 in previous studies for several of the investigated molecules.^[17,19,48] This finding is also in
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33 agreement with the large solvent effect on the fluorescence quantum yields of these molecules
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35 (see the Supporting Information, Tables S11-S13). The emission is strongly quenched in the
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37 most polar solvents, where intramolecular charge transfer processes possibly accompanied by
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39 twisting of the molecular structure and consequent non-radiative deactivations to the ground
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41 state by internal conversion are favored.
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50 It has to be noted that the absorption spectral shifts observed when passing from one molecule
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52 to another in this series could be well predicted by using the simple Kuhn's model^[50] (see the
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54 Supporting Information and in particular Table S14). This model considers the π -electrons of the
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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.

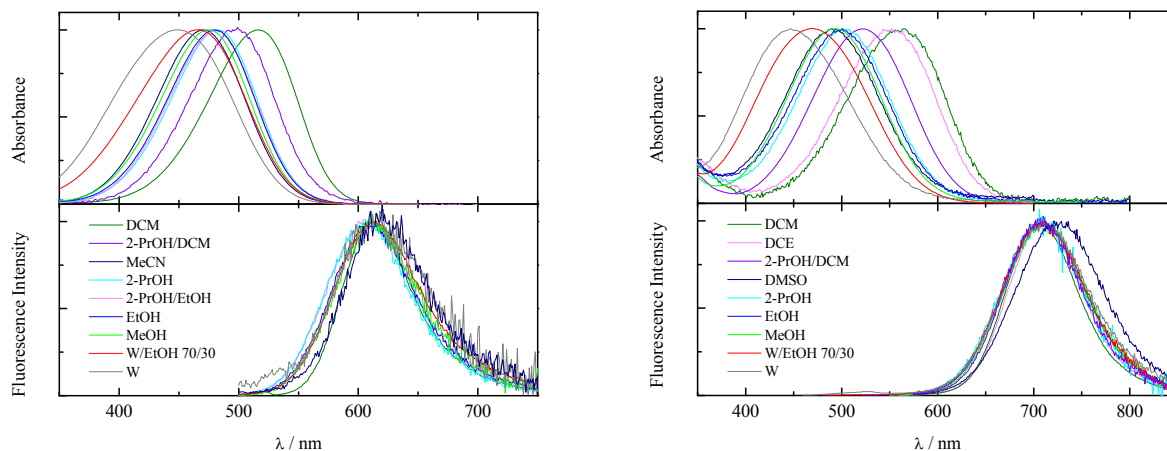


Figure 1. Normalized absorption and emission spectra of **5** (left) and **6** (right) in solvents of different polarity.

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

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 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 by using the Reichard equation (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 (β_{CT}) and frequency independent (β_0) hyperpolarizabilities, evaluated through the Oudar equations (2) and (3) are generally negative.^[21] The absolute values of β_{CT} and β_0 are reported in Table 2. The β_{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⁺– π –Donor systems is differently influenced by the nature of the electron acceptor portion, the electron donor group and the π –bridge. The comparison among the frequency independent β_0 values (Table 2) allows for meaningful structure–property considerations for these cationic chromophores. A longer π –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) dibuthylamino phenyl (donor unit) derivatives showing an ethylene or a butadiene π –bridge.^[51] A more conjugated and larger electron acceptor moiety (quinolinium vs. pyridinium) also has a positive impact on the

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3 hyperpolarizability (e.g. $\beta_0 = 44 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$ for **1**, *o*-**PiEtDMA** vs. $\beta_0 = 82 \times 10^{-30} \text{ esu}^{-1}$
4 cm^5 for **3**, *o*-**QuiEtDMA**; $\beta_0 = 120 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$ for **2**, *o*-**PiButDMA** vs. $\beta_0 = 160 \times 10^{-30}$
5 $\text{esu}^{-1} \text{ cm}^5$ for **4**, *o*-**QuiButDMA**).^[51] Additionally, it was found that a more conjugative position
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7 of attachment for the pyridinium electron acceptor portion (*para* vs. *ortho*) causes an increase in
8 the hyperpolarizability of these molecules (e.g. $\beta_0 = 44 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$ for **1**, *o*-**PiEtDMA** vs.
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10 $\beta_0 = 75 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$ for **5**, *p*-**PiEtDMA**; $\beta_0 = 120 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$ for **2**, *o*-**PiButDMA** vs.
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12 $\beta_0 = 200 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$ for **6**, *p*-**PiButDMA**). All these results unambiguously show a
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14 significant increase in the hyperpolarizability of these chromophores upon increasing their
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16 molecular conjugation. As clearly shown in Table 2, the β_0 value indeed increases upon
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18 increasing the oscillator strength and upon red shifting of the absorption spectrum.
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27 On the other hand, other comparisons among the β_0 values reported in Table 2 uncover the role
28 played by the electron donor and the electron acceptor units in affecting the hyperpolarizability.
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30 When comparing two similar structures characterized by a different electron donor group
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32 (dimethylamino vs. diphenylamino) the two beta values are surprisingly found equal (e.g. $\beta_0 = 44$
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34 $\times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$ for **1**, *o*-**PiEtDMA** vs. $\beta_0 = 45 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$ for **8**, *o*-**PiEtDPA**). Similarly,
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36 a change in the electron acceptor unit by adding a cyano group to the methylpyridinium
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38 chromophore, which thus does not significantly affect the molecular conjugation, has only a little
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40 positive effect on the hyperpolarizability (e.g. $\beta_0 = 120 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$ for **2**, *o*-**PiButDMA** vs.
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42 $\beta_0 = 140 \times 10^{-30} \text{ esu}^{-1} \text{ cm}^5$ for **7**, *o*-**PiCNButDMA**). These findings suggest that a change in the
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44 electron donor/electron acceptor group nature that does not affect the molecular conjugation
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46 (unchanged absorption spectrum) has a negligible/little impact on the hyperpolarizability of the
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48 investigated push-pull systems. This is consistent with literature reports showing that an increase
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in donor/acceptor group strength does not necessarily leads to an enhancement of the hyperpolarizability.^[52]

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).

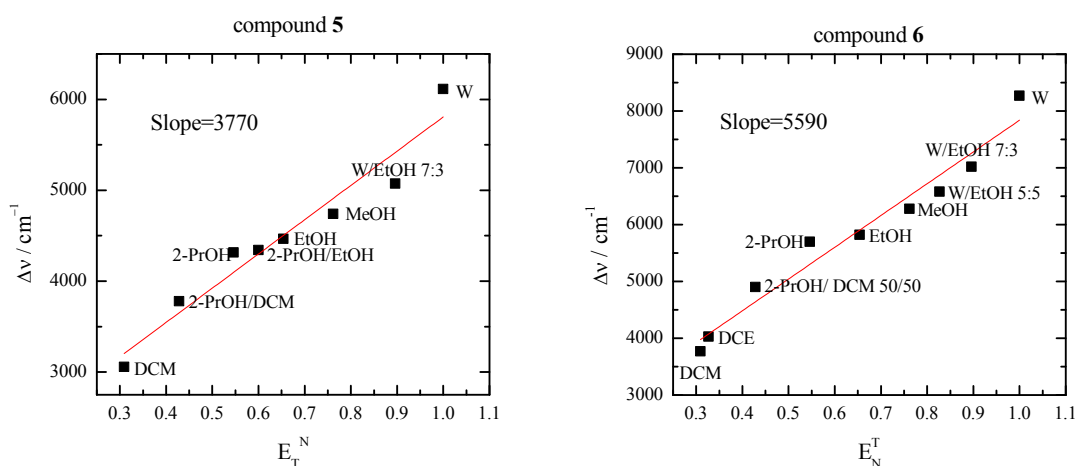


Figure 2. Plot of the Stokes shift as a function of E_T^N parameter for **5** and **6**.

Table 2. Calculated parameters (μ_g , $\mu_{e,FC}$ and a) for the most stable rotamer of the investigated compounds and experimental parameters (ν_{eg} , f , β_{CT} and β_0) derived from its solvatochromism using Eqs. (1) and (2).

Comp.nd	μ_g / D	$\mu_{e,FC}$ / D	a / 10^{-8} cm	slope	$\Delta\mu_{exp}$ / D	ν_{eg} / cm^{-1}	f	β_{CT} / 10^{-30} esu $^{-1}$ cm 5	β_0 / 10^{-30} esu $^{-1}$ cm 5
1	6.86 ^a	3.30 ^a	8.18	3270	-7.33	20660	0.648	320	44
2	9.9 ^b	2.6 ^b	9.60	5260	-11.8	19305	0.873	2930	120
3	1.6 ^b	9.4 ^b	9.57	1850	-6.98	18050	0.847	1330	82
4	2.9 ^b	8.5 ^b	11.0	4650	-13.6	16580	0.657	824	160
5	13.34	0.13	8.8	3770	-8.8	19340	0.756	1770	75
6	17.85	1.29	10.1	5590	-13.2	17953	1.068	2840	200
7	13.55	8.43	9.59	4180	-10.5	17153	0.820	988	140
8	10.28 ^c	3.66 ^c	9.3	2301	-7.5	20637	0.652	335	45
9	19.02	10.20	10.2	3450	-10.5	18020	0.752	1710	110
10	14.62 ^a	4.94 ^a	8.15	3900	-7.97	25640	0.605	58	23
11	15.0 ^d	4.50 ^d	8.19	3790	-8.0	26667	0.618	48	21
12	18.26 ^a	4.55 ^a	8.60	2910	-7.46	21650	0.531	159	32

^acalculated in DCM from ref. 17 ^bcalculated in DCM from ref.19 ^ccalculated in DCM from ref. 53 ^dcalculated in DCM from ref. 20.

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 low 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

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3 excited state absorption band, peaked around 550 nm for **5** and 600 nm for **6** respectively, is
4 formed at early delays after excitation and subsequently decays. Below 520 nm the tail of the
5 ground state absorption is clearly visible in the case of **5**. For both dyes as well as for all the
6 other investigated systems (see Figure S23 for **7** and **9** in MeOH and refs 17–20), a large red
7 shift in time of the stimulated emission band is observed during these measurements which could
8 be consistent with both relaxation processes and population dynamics to a lower energetic
9 excited state. The global fitting of the acquired data revealed for **5** and **6** the presence of three
10 and four exponential components, respectively (see panel C of Figure 3 and Table S15). The first
11 two components of hundreds of femtoseconds and few picoseconds perfectly match the
12 well-known time constants for the inertial and diffusive solvation in MeOH. The last component
13 characterized by a lifetime of 22 ps and 250 ps for **5** and **6**, respectively, is assigned to the fully
14 relaxed lowest excited singlet state, which shows an intramolecular charge transfer character –
15 S_1 (ICT). The presence of two distinct emissive minima in the excited states of several molecules
16 under investigation here – a low dipole moment intermediate locally excited state and a high
17 dipole moment relaxed ICT state – has been observed in previous experimental and theoretical
18 studies by our research group. [17,19,48] In the case of **6**, an intermediate transient with a lifetime of
19 27 ps is indeed also found. This component can be associated to the low dipole moment excited
20 state reached by light absorption – S_1 (LE). This S_1 (LE) state, which for **6** is observed as a
21 separate component, shows instead a lifetime shorter than solvent relaxation in the case of **5**. [17]
22 The photoinduced intramolecular charge transfer is therefore fast, faster than solvation when the
23 π -bridge is an ethylene and slow, slower than solvation when the π -bridge is a butadiene. This
24 result suggests that the effect of a longer π -bridge is to slow down the intramolecular charge
25 transfer in these cationic molecules.
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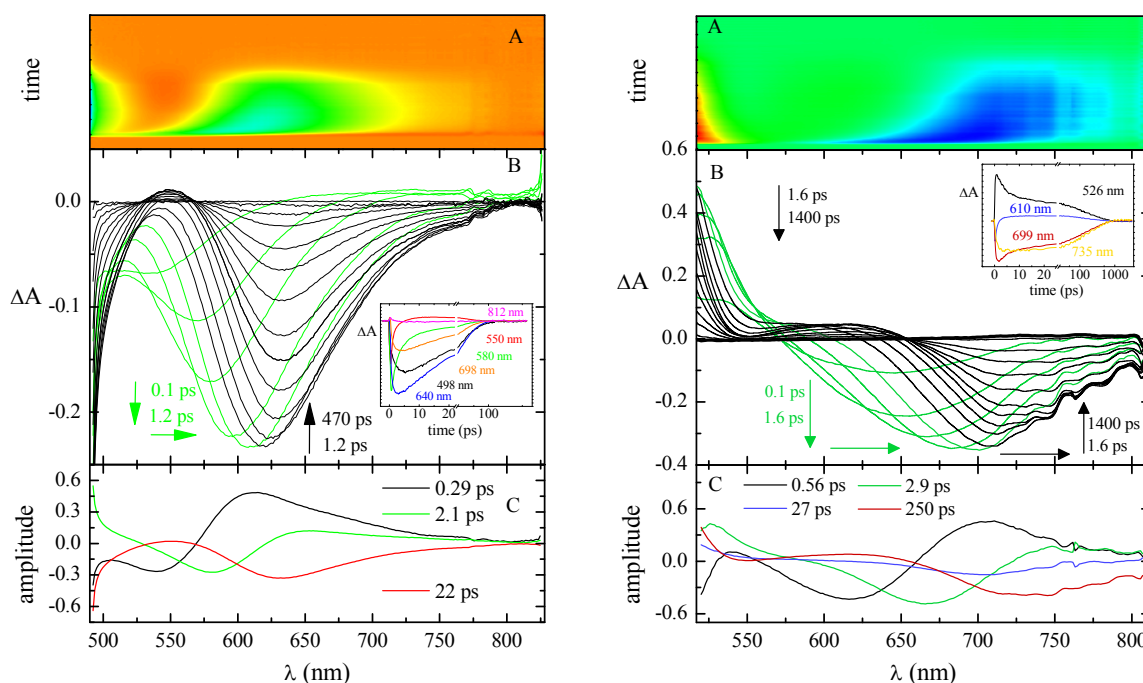


Figure 3. Femtosecond transient absorption data of compounds **5** (left) and **6** (right) in MeOH.

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

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3 S18). Moreover, previous studies from our group about compounds **1** and **10**^[25] have shown that
4 a highly viscous medium, such as a hydrogel, is able to completely inhibit the formation of the
5 final relaxed ICT state thus strongly confirming its TICT nature. In general, the excited state
6 deactivation investigated by ultrafast transient absorption becomes faster upon increasing the
7 solvent polarity. In particular, the lifetime of the relaxed intramolecular charge transfer state
8 $-S_1(\text{ICT})-$ is significantly shortened when passing from the low polar solvent DCM to the polar
9 MeOH and W (see Tables S15–S17). The amount of quenching of this lifetime (τ_{ICT}) with the
10 solvent polarity can be quantified according to simple equations ($\tau_{\text{ICT,DCM}}/\tau_{\text{ICT,MeOH}}$ or $\tau_{\text{ICT,DCM}}$
11 $/\tau_{\text{ICT,W}}$) and can be considered an indication of the excited state ICT degree for these molecules
12 (Table 3).
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27 The large series of molecules here investigated provides a basis for insightful comparisons and
28 considerations about structure–property relationships as related to their photoinduced ICT degree
29 (Table 3). First of all, looking at Table S15, it is apparent that a stronger degree of quenching is
30 obtained when considering an ethylene (5.6 and 12 when passing from DCM to MeOH for **1**,
31 *o*-**PiEtDMA** and **5**, *p*-**PiEtDMA**, respectively) with respect to a butadiene π -linker (2.8 and 3.2
32 for **2**, *o*-**PiButDMA** and **6**, *p*-**PiButDMA**, respectively). A longer π -bridge has a significantly
33 negative effect on the intramolecular charge transfer efficiency in these molecules. A second
34 important observation can be deduced by looking at Table S16. A quenching of 5.6 times is
35 observed when passing from DCM to MeOH for **1**, *o*-**PiEtDMA**. When replacing the
36 pyridinium electron acceptor moiety with a quinolinium (**3**, *o*-**QuiEtDMA**) or when replacing
37 the dimethylamino donor group with a diphenylamino (**8**, *o*-**PiEtDPA**) or both (**9**,
38 *o*-**QuiEtDPA**), a same quenching degree of 9.1 is found. This result demonstrates that the ICT
39 efficiency is enhanced by employing a stronger electron donor group (diphenylamino vs.
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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 bring about opposite effects, with the former having a negative impact on the ICT efficiency, whereas the latter exerts a positive influence.

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) ^a	5.6	2.8	9.1	5	12	3.2	10	9.1	9.1	2.1	1	1.4
quenching degree (DCM-W) ^b	30	10	38	16	23	10	19	32		7.1		1.5

^a $\tau_{\text{ICT,DCM}} / \tau_{\text{ICT,MeOH}}$; ^b $\tau_{\text{ICT,DCM}} / \tau_{\text{ICT,W}}$.

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 a low polar solvent 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

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3 sections (δ_{TPA}), obtained here by the comparative method, are reported in Table 4, as evaluated at
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5 an excitation wavelength roughly correspondent to the double of the corresponding linear
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7 absorption maximum.
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11 The obtained results demonstrate the important effect of both the molecular conjugation and
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13 the ICT degree on this non-linear optical property. The two-photon cross section is doubled
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15 when an ethylene spacer ($\delta_{\text{TPA}}=51$ GM for **1**, *o*-**PiEtDMA**) is replaced with a butadiene spacer
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17 ($\delta_{\text{TPA}}=106$ GM for **2**, *o*-**PiButDMA**). Also, the two-photon cross section is enhanced by almost
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19 a factor of five when the position of attachment of the pyridinium acceptor unit is changed from
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21 *ortho* ($\delta_{\text{TPA}}=51$ GM for **1**, *o*-**PiEtDMA**) to *para* ($\delta_{\text{TPA}}=230$ GM for **5**, *p*-**PiEtDMA**). These
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23 findings show the strong positive impact of an increase in molecular conjugation on the
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25 two-photon absorption response. At the same time, a significant increase (by three times) in
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27 two-photon absorption is observed when replacing the dimethylamino donor ($\delta_{\text{TPA}}=51$ GM for **1**,
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29 *o*-**PiEtDMA**) with a diphenylamino group ($\delta_{\text{TPA}}=150$ GM for **8**, *o*-**PiEtDPA**) or when replacing
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31 the pyridium acceptor ($\delta_{\text{TPA}}=51$ GM for **1**, *o*-**PiEtDMA**) with a quinolinium ($\delta_{\text{TPA}}=145$ GM for
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33 **3**, *o*-**QuiEtDMA**). Also, the two-photon cross section is more than doubled by adding a cyano
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35 group ($\delta_{\text{TPA}}=250$ GM for **7**, *o*-**PiCNButDMA**) to the electron deficient pyridium moiety
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37 ($\delta_{\text{TPA}}=106$ GM for **2**, *o*-**PiButDMA**). These findings show the positive impact of a stronger
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39 electron donor/acceptor couple and enhanced ICT degree on this non-linear optical property.
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Table 4. Two photon absorption cross sections of the investigated compounds in DCM at the excitation wavelength roughly correspondent to the double of their linear absorption maxima.

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

Discussion

In this investigation, steady state and time resolved spectroscopy, with both nanosecond and femtosecond time resolution, have been employed to obtain information about the non-linear optical (NLO) properties (hyperpolarizability and two-photon absorption) of a large series of structurally analogous push-pull dipolar cationic chromophores (Acceptor⁺- π -Donor). Our findings are summarized in Figure 4. In the figure, the frequency independent hyperpolarizability (β_0) as evaluated by the solvatochromic method, and the two-photon absorption cross section (δ_{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 non-linear optical properties of organic molecules.^[23,28] 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.

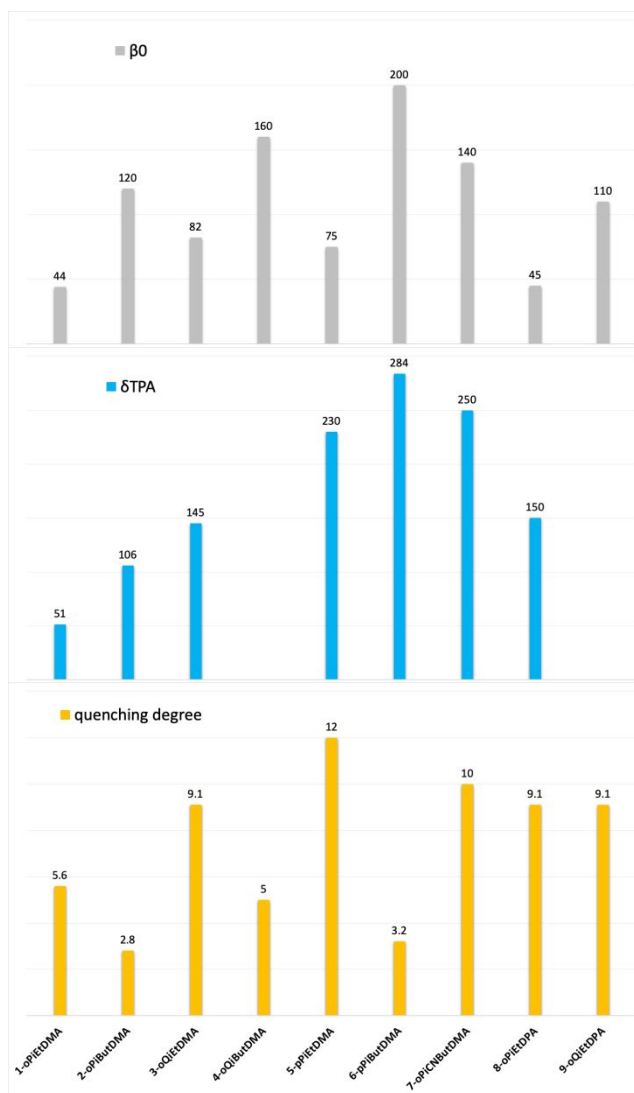


Figure 4. Static hyperpolarizability (β_0 in $10^{-30} \text{ esu}^{-1} \text{ cm}^5$), two photon absorption cross section (δ_{TPA} in GM) and quenching degree upon increasing solvent polarity ($\tau_{\text{ICT,DCM}} / \tau_{\text{ICT,MeOH}}$) for the investigated compounds.

We found that both the molecular conjugation and the intramolecular charge transfer character of the excited states strongly influence the non-linear optical response. However, the two considered non-linear 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 is surprisingly almost unaffected by the excited state

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3 intramolecular charge transfer degree as evaluated from the ultrafast dynamics. Differently, the
4 two-photon absorption cross sections are strongly enhanced by both a conjugation and an
5 intramolecular charge transfer degree increase. Whether the excited state intramolecular charge
6 transfer degree of these chromophores increases or decreases, the hyperpolarizability and
7 two-photon absorption cross section show an increase upon increasing the molecular
8 conjugation. On the other hand, if the system conjugation is not changed, the effect of the
9 intramolecular charge transfer degree is extremely important on the two-photon absorption but
10 practically negligible on the hyperpolarizability.
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26 **Conclusions**

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29 This study represents a successful attempt to uncover structure-property relationships for two
30 non-linear optical properties (first hyperpolarizability and two-photon absorption cross section)
31 in a large series of push-pull cationic chromophores. In these dipolar Acceptor⁺- π -Donor dyes
32 the nature of the donor and acceptor units and that of the π -linker were synthetically tuned,
33 allowing important comparisons among the molecules to be drawn. We found a strong increase
34 in hyperpolarizability upon increasing the molecular conjugation, whereas the
35 hyperpolarizability is almost unaffected by an increase in the donor/acceptor strength.
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46 Differently, an enhancement in the two-photon absorption cross sections is observed in these
47 dyes upon increasing both their conjugation and intramolecular charge transfer degree. Our
48 investigation thus reports a large group of new, interesting and low-cost organic materials for
49 applications in non-linear optics showing significant responses. Most importantly, our results
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3 offer accurate guidelines regarding the crucial structural features to be considered when
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5 designing organic systems with large hyperpolarizability or two-photon absorption cross section.
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10 11 12 ASSOCIATED CONTENT

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15 **Supporting Information.** Absorption and emission spectra for all the investigated compounds in
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17 different solvents as well as plots of the Stokes shifts vs. the E_T^N parameter; fluorescence
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19 quantum yields; femtosecond transient absorption results; computational results.
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25 26 AUTHOR INFORMATION

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34 35 **Author Contributions**

36
37 The manuscript was written through contributions of all authors. All authors have given approval
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39 to the final version of the manuscript.
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5 state solvatochromic investigation.
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