Evaluation of Hyperpolarizability from the Solvatochromic Method: Thiophene Containing Push−Pull Cationic Dyes as a Case Study.

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ABSTRACT We report here a successful attempt to test a solvatochromic method to estimate the hyperpolarizability (β) of cationic push–pull chromophores. This represents a simple method, alternative to the sophisticated spectroscopic techniques often employed, which can be easily and quickly applied through equipment commonly available in a typical chemistry laboratory. The case–study taken into consideration consists of nine donor–π−acceptor derivatives exhibiting the rarely observed negative solvatochromism. In these dyes the electron acceptors are positively charged methyl pyridinium or quinolinium rings and the electron donors are electron rich thiophene rings eventually coupled with the strongly electron donating dibuthylamino group or pyperidine. The obtained β values are enhanced in this molecular series upon increasing molecular dimensionality and conjugation as well as by increasing the donor/acceptor strength. The highest hyperpolarizability is estimated for the chromophore bearing methyl quinolinum and pyperidine where the most efficient photoinduced intramolecular charge transfer is also revealed by means of state–of–the–art femtosecond transient absorption measurements.

Introduction

During the last decade materials showing non−linear optical (NLO) properties have been the object of increasing attention because of their impactful applications in different fields such as communications and medicine. Even though inorganic systems are currently widely employed materials for electro−optical devices, organic chromophores are particularly interesting candidates for elaboration of optimized NLO materials because of their notable chemical flexibility, easy and inexpensive preparation. A large number of studies have been dedicated to molecular engineering chromophores that exhibit enhanced quadratic hyperpolarizabilities (β) for the design of efficient second order NLO devices.[1] In particular, much effort has been devoted to the optimization of the push−pull typical structure: molecules that bear an electron donating group and an electron withdrawing group linked through a π−conjugated system.[2,3] Cationic chromophores have shown to be really promising as electron deficient moieties, not only for their significant electron withdrawing ability but also for their water solubility which is really appealing for their possible biological and medical applications.[4,5]

The common technique for measuring molecular second order polarizabilities is Electric Field Induced Second Harmonic Generation (EFISH).[6] In this method a DC electric field is applied across a solution of the compound to be tested, a laser beam is passed through the solution and the intensity of the generated second harmonic light is measured. Elaborated and expensive instruments are required to carry out these time−consuming measurements. Moreover, the widely used EFISH technique is essentially inoperable for measuring the second order response of isolated charged molecules, due to ion migration towards the electrodes and related cancellation of the poling field.[1]

In the last few years the interest of our research group has been mainly addressed to the study of the solvent effect on the spectra, photophysics and excited state dynamics of donor−acceptor organic systems exhibiting photoinduced intramolecular charge transfer (ICT) phenomena. At first, neutral dipolar donor−π−acceptor systems showing positive fluorosolvatochromism have been considered.[7−9] Lately, our attention has been largely devoted to the study of cationic chromophores characterized by the less common negative solvatochromism.[10,11] The most promising investigated systems hold methyl pyridinium or methyl quinolinium as electron deficient portion, aromatics (such as pyrene or naphthalene) as electron rich portions or dimethyl amino/diphenyl amino groups as strongly electron donating groups and ethylene bridges as π−spacers.[12−15] In our latest work,[16] cationic dyes bearing thiophenes as electron rich π−linkers have been investigated and their Two−Photon Absorption cross sections interestingly resulted very high. Thiophene containing methyl pyridinium and methyl quinolium derivatives have also shown a remarkable capability of binding DNA in previous investigations carried out in our laboratory[17] as well as an important antiproliferative activity during in vitro testing.[18]

The goal of the present work is thus to devise and test a simple method, alternative to the sophisticated EFISH spectroscopy, for determining second order polarizabilities of push−pull cationic systems from their solvatochromism, that is the solvent polarity effect on their stationary absorption and emission spectra. This solvatochromic method can be easily and quickly employed, by exploiting equipment commonly available in a typical chemistry laboratory. The described experimental procedure, previously elaborated for neutral molecules exhibiting positive fluorosolvatochromism,[19−21] is now tentatively tuned to estimate hyperpolarizability also in the case of isolated cationic chromophores. The case study taken into consideration in the present work is a series of donor−π−acceptor dyes expected to show remarkable NLO response,[22−26] where the electron acceptors are methyl pyridinium or methyl quinolinium rings and the electron donors thienyl or bithienyl aromatics (compounds **A**−**E** in Chart 1) eventually coupled with the strong dibuthyl amino group or pyperidine (compounds **F**−**I** in Chart 1). Valuable information about the ICT occurring during the excited state dynamics of these push−pull compounds was obtained by state−of−the−art femtosecond transient absorption measurements in the UV−visible spectral range, allowing the NLO properties (β coefficient) evaluated for these organic dyes to be interpreted and discussed in connection with their photoinduced ICT efficiency.

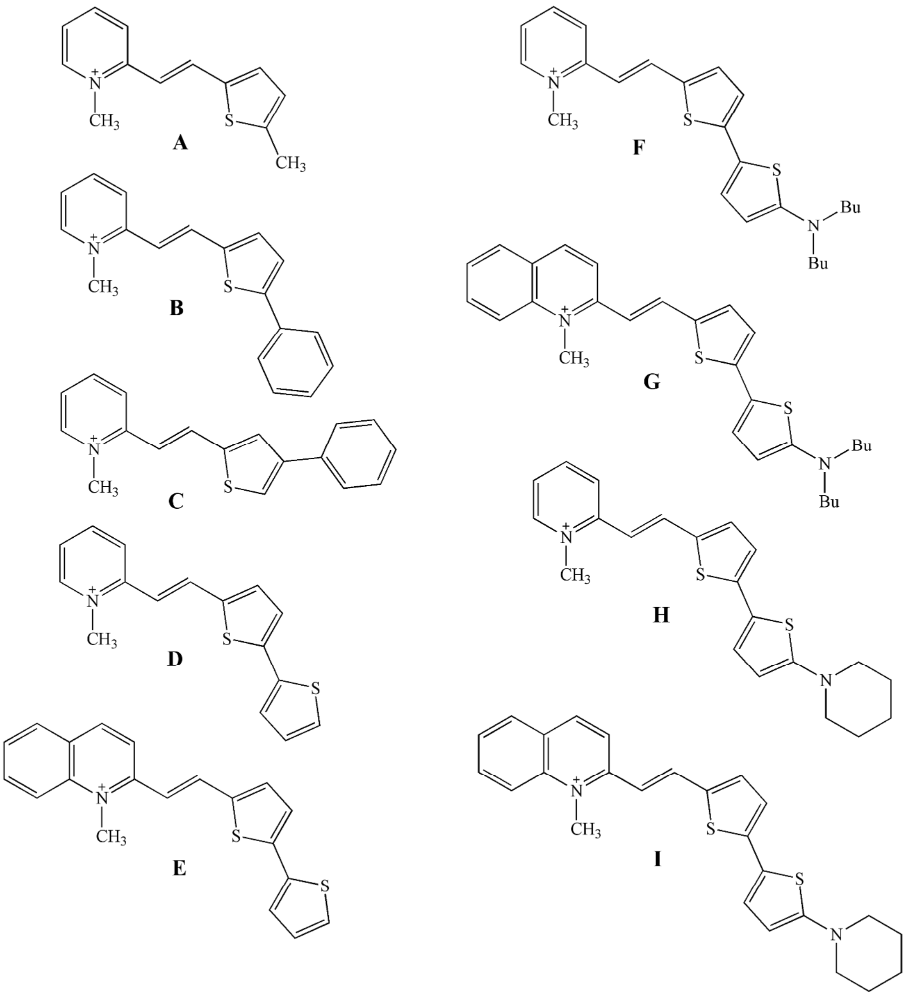

Chart 1. Molecular structures of the investigated compounds.

Experimental Section

Chemicals. The investigated compounds (**A**−**I**, shown in Chart 1) were synthesized following previously reported procedures.[18,25] Measurements were performed in various solvents (Fluka, spectroscopic grade): chloroform ($CHCl_3$), 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 ± 10%) was determined at λ_{exc} corresponding to the maximum of the first absorption band. Tetracene (ϕ_F = 0.17[27] in aerated CH) was used as fluorimetric standard.

The experimental setup for femtosecond transient absorption measurements has been widely described elsewhere.[28−30] 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 Glotaran software.[31]

Computational details. Quantum−mechanical calculations were carried out using the Gaussian 09 package.[32] 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.[33,34] 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).[35] Atomic charges and dipole moments were obtained by use of the quantum theory of atoms in molecules (QTAIM)[36] Calculations were carried out on molecular structures with the C_4H_{10} groups replaced by the CH_3 ones for chromophores **F** and **G**. Calculations were carried out on the most stable conformation, that is the s–*trans* conformation (as for the ethylenic double bond with respect to the thiophene, shown in Chart 1) for all of the investigated compounds. The bithienyl groups in the most stable conformer of **D−I** are in all cases in anti–configuration.

β_{CT} and the product of electric dipole moment and first dipole hyperpolarizabily were calculated at the CAM-B3LYP/6-31+G*/PCM level of theory by including local field effects, according to previous studies of some of the present authors.[26,37-39]

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:[40,41]

$$\Delta\upsilon = \upsilon_A - \upsilon_F = 11307.6\frac{\Delta\mu^2 a_D^3}{\Delta\mu_D^2 a^3}E_T^N + \text{const} \qquad (1)$$

where $\Delta\upsilon = \upsilon_A - \upsilon_F$ 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 for the 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[42] 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 $\Delta\upsilon$ 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:[43,20]

$$\beta_{\text{CT}} = \beta_{\text{zzz}} = \frac{3}{2h^2c^2} \times \frac{\upsilon_{\text{eg}}^2 r_{\text{eg}}^2 \Delta\mu}{(\upsilon_{\text{eg}}^2 - \upsilon_L^2)(\upsilon_{\text{eg}}^2 - 4\upsilon_L^2)} \qquad (2)$$

where r_{eg} is the transition dipole moment, υ_{eg} is the transition frequency (in cm^{-1}, assumed to be the maximum of the bathochromic absorption band) and υ_L is the frequency of the reference incident radiation (chosen as 1907 nm, for comparison purposes with experimental EFISH data) to which the β value would be referred. The r_{eg} value is related to the oscillator strength (f) by $r_{\mathrm{eg}}^2 = \frac{3e^2h}{8\pi^2\mathrm{mc}} \times \frac{f}{\upsilon_{\mathrm{eg}}} = 2.13 \times 10^{-30} \times \frac{f}{\upsilon_{\mathrm{eg}}}$ (with f being obtained from the absorption integrated band as $f = 4.32\times10^{-9}\int\varepsilon(\upsilon)d\upsilon$).[44]

The method based on the solvent effect on the spectra contains several approximations, thus allowing only an 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. This 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 EFISH.

The static hyperpolarizability, whose value is instead frequency independent, can be defined as follows:[45]

$$\beta_0 = \frac{3}{2h^2c^2} \times \frac{r_{\mathrm{eg}}^2 \Delta\mu}{\upsilon_{\mathrm{eg}}^2} \qquad (3)$$

Results and Discussion

Solvatochromism and Hyperpolarizability

Absorption and emission spectra of compounds **A−I** have been recorded in several solvents of different polarities. In particular, chlorinated solvents of low/medium polarity (such as $CHCl_3$, DCM and DCE), protic polar solvents (such as 2−PrOH, EtOH, MeOH and W) and aprotic polar solvents (such as Ac, DMSO and MeCN) have proved to be able to effectively dissolve these cationic dyes. Mixtures of the aforementioned solvents have been also used to provide additional media where the polarity could be finely tuned. The investigated salts are considered completely dissolved as free ions surrounded by solvent without any clear evidence of ion-pair formation. In previous detailed studies on analogous methyl pyridinium derivatives, the presence of ion-pair was evidenced in solvents of $E_T^N < 0.3$.[12,47] On the basis of this result, some contribution of ion pairs could be expected only in $CHCl_3$ ($E_T^N = 0.259$). In fact, some anomalies found in the behavior of the investigated dyes in $CHCl_3$, such as the blue shift of the absorption maximum with respect to DCM or a unexpectedly too low ϕ_F (see below), could be related to partial contribution of ion-pairs.

The absorption spectra of the dyes containing the electro–deficient methyl pyridinium/quinolinium and electron rich aromatic rings such as thiophene and benzene (compounds **A**−**E**) are placed in the high energetic portion of the visible spectral region that is between 350 and 550 nm (see Figure 1 and Figures S1, S4, S7, S11 in the Supporting Information). The solvent effect on the absorption maximum position is remarkable: the absorption spectrum is significantly shifted toward the blue upon increasing the solvent polarity. The trend of the maximum wavelength position with the E_T^N parameter for the solvent polarity is apparent when chlorinated and protic solvents are considered (see Table 2 and Tables S1, S3, S5, S8 in the Supporting Information), as reported in the literature for other methyl pyridinium derivatives.[46] The observed negative solvatochromism of the absorption is in agreement with the reduction of the dipole moment predicted by the quantum mechanical calculations for these push−pull cationic chromophores when going from the ground to the Frank−Condon excited state (see below, Table 3). In fact, the positive charge is localized on the methyl pyridinium/quinolinium in the ground state with this being the cause for its large dipole moment.

Upon light absorption a charge transfer takes place from the electron rich aromatic rings toward the positively charged methyl pyridinium/quinolinium, determining a positive charge which is possibly delocalized across the entire molecular structure in the Frank−Condon excited state. This latter then becomes a state characterized by a lower dipole moment.

The emission spectra for compounds **A**−**E** are substantially unaffected by the solvent polarity (see Figure 1 and Figures S1, S4, S7, S11 in the Supporting Information). The fluorescence spectra are not much influenced by the solvent, with the emission maximum position being just slightly blue–shifted in the solvents of highest polarity and in the most viscous solvents (such as 2−PrOH and DMSO). Fluorescence excitation spectra for all these dyes showed a remarkable overlapping with the absorption, as shown in the Supporting Information (Figure S10) in the case of compound **D** as a representative example.

The solvatochromic effect investigated on the absorption and emission spectra of these dyes has allowed the solvent effect on the Stokes−shift to be evaluated. The plot of the Stokes shift as a function of the solvent E_T^N parameter is reported in Figure 2 and in the Figures S2, S5, S8 and S12 of the Supporting Information. From the slope of the linear fitting in these graphs the difference between the dipole moments of the excited Frank−Condon and the ground state ($\Delta\mu$) has been calculated according to the Reichardt equation (1). The Reichardt model[48,40,41] considering the E_T^N parameter to express solvent polarity was used as it was found to give the best alignment of the experimental data with respect to other methods to rationalize the solvatochromic shifts.[49−51] The obtained $\Delta\mu$ values (reported in Table 3) reflect the dipole moment reduction occurring during light absorption for these chromophores and are found to be enhanced in modulus upon increasing molecular conjugation and dimensionality, that is when going from compound **A** ($\Delta\mu = -5.43$ D) to compound **E** ($\Delta\mu = -9.84$ D).

The fluorescence quantum yields measured for the thiophene containing compounds **A**, **D** and **E** are generally quite low, being of the order 10^{-2}−10^{-4} depending on the structure and the solvent (see Table 1 and Tables S1 and S8 in the Supporting Information). The fluorescence efficiency is generally enhanced upon increasing the molecular dimensionality and conjugation: for instance ϕ_F measured in DCM shows values of 0.0003 for **A** (structure composed of a methyl pyridinium and one thiophene), 0.0017 for **D** (composed of a methyl pyridinium and two thiophenes) and 0.011 for **E** (characterized by the presence of a methyl quinolinium and two thiophenes). The fluorescence quantum yield is generally decreased upon increasing the solvent polarity; this behavior has often been observed for push−pull systems[12−14] and is particularly evident in the case of compound **E** (see Table S8). The *trans*−*cis* photoisomerization quantum yield has been found to be remarkable for compounds **A**, **D** and **E** (see Table 1 and Tables S1 and S8 in the Supporting Information). The obtained results suggest that the photoreaction is the main deactivation pathway for the excited states of these thiophene containing push−pull chromophores. It is possible that the photoisomerization takes place involving either an excited triplet or an excited singlet mechanism. Population of the lowest excited triplet state and therefore a not negligible inter system crossing has been indeed revealed during the femtosecond transient absorption measurements on these **A**−**E** dyes (see discussion below and results reported in Table 5).

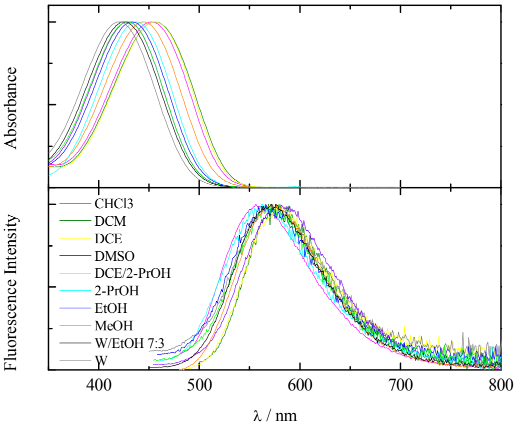

Figure 1. Normalized absorption and emission spectra of compound **D** in solvents of different polarity.

Table 1. Absorption and emission properties of compound **D** in solvents of different polarity (expressed as E_T^N parameter).

Solvent	E_T^N	λ_{abs} / nm	λ_{em} / nm	$\Delta\upsilon$/cm^{-1}	ε /M^{-1} cm^{-1}	ϕ_F	$\phi_{trans\rightarrow cis}$
$CHCl_3$	0.259	453	560	4220		0.0008	
DCM	0.309	457	581	4670	23500	0.0017	0.13
DCE	0.327	456	579	4660		0.0041	
DCE/PrOH 5:5	0.436	446	572	4940			
DMSO	*0.441*	*430*	*581*	*6040*		*0.0060*	
2−PrOH	0.546	437	562	5090		0.0028	
EtOH	0.654	433	566	5430		0.0027	
MeOH	0.762	428	579	6090		0.0017	
W/EtOH 5:5	0.827	428	569	5790			
W/EtOH 7:3	0.896	425	572	6050			
W	1	421	574	6330		0.0019	

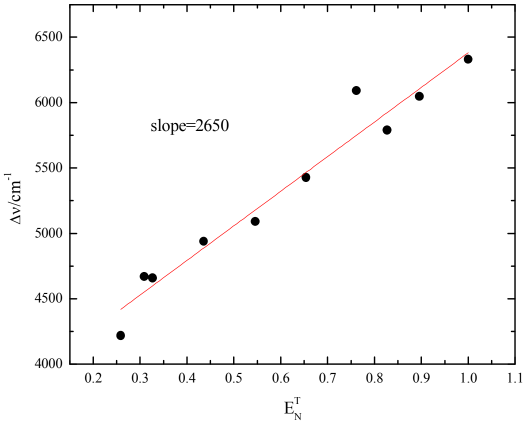

Figure 2. Plot of the Stokes shift (Δυ) as a function of the E_T^N parameter for compound **D**.

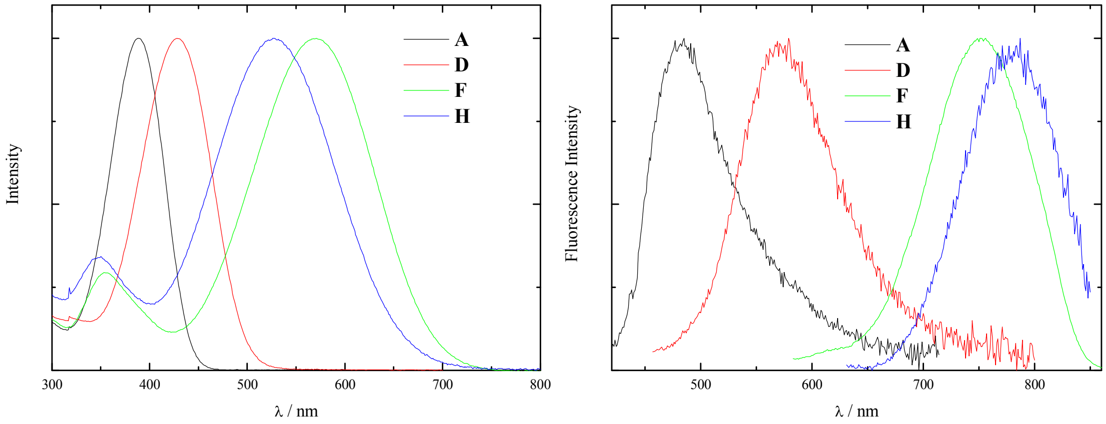

Figure 3. Normalized absorption and emission spectra of compounds **A**, **D**, **F** and **H** in MeOH.

Figure 3 shows the significant red shift observed on both the absorption and the emission spectra when the molecular conjugation is increased by adding to the molecular structure a further thiophene ring that is by passing from compound **A** to compound **D**. It is noteworthy that this bathchromic shift becomes very apparent when the molecular structure is further complicated by the presence of additional strongly electron donor moieties such as a dibuthyl amino group (compound **F**) or a pyperidine (compound **H**). For these chromophores the absorption spectra are very broad and interestingly placed in the red portion of the visible spectral region. These findings make the latter compounds particularly appealing as potential light absorbers and photosensitizers in organic photovoltaic solar cells and as NIR emitters. Indeed, the fluorescence spectra of these compounds are located in the far red of the visible and in the near infrared spectral window, which is not very common for organic emitters.

The absorption spectra of compounds **F−I** (see reference 16, Figure 4, Figures S14 and S16 and S18 in the Supporting Information) are strongly shifted toward higher energies (negative solvatochromism) when the solvent is changed from a low polar (such as $CHCl_3$ or DCM) to a highly polar one (such as MeOH or W). A little blue shift with solvent polarity has also been observed for the emission spectra of **F−I**. The observed solvatochromism of the absorption spectra is in good agreement with the results of the quantum mechanical calculations for the ground and excited Frank−Condon state dipole moments (Table 3). In the case of compound **F**, a complete theoretical investigation concerning also the relaxed excited state properties was previously carried out.[16] No significant difference between the dipole moments of the Frank−Condon state and the relaxed excited state was found: the emission predicted to take place from a low polar state and leading the molecule back to its highly polar ground state might give a possible explanation for the small negative fluorosolvatochromism experimentally observed. Fluorescence quantum yields for **F−I** are generally very low and slightly reduced upon increasing the solvent polarity. Photoisomerization efficiencies for these chromophores are negligible as well as triplet production,[16] as evidenced also by the femtosecond transient absorption measurements (Tables 6 and 7). These findings suggest that for these strongly push−pull compounds the excited state decay pathway competitive with fluorescence is internal conversion to the ground state. Very interestingly, analysis according to the Reichardt equation of the Stokes shift vs. E_T^N plots (see Figure 5 and Figures S15 and S17 and S19 in the Supporting Information) for these compounds bearing effective electron donor portions has resulted in very high $\Delta\mu$ values (Table 3).

The difference between the dipole moments of the excited and ground state ($\Delta\mu$) for compounds **A−I** estimated from their solvatochromism has been used to obtain the frequency dependent hyperpolarizability (β_{CT}) through the Oudar equation (2) and its static frequency independent analogue (β_0) through equation (3). The values of β obtained by the solvatochromic method for the cationic dipolar chromophores under investigation are reported in Table 3. The $\Delta\mu$ values are considered to be negative in agreement with the decrease of the dipole moment predicted to take place upon light absorption. For this reason the computed β values are negative, as it was previously reported in the literature for negatively solvatochromic merocyanine dyes.[52] The absolute values of β_{CT} are reported in Table 3, which have been computed by taking into account the frequency of the exciting laser (corresponding wavelength of 1907 nm) used in EFISH experiments carried out on compounds **B**, **C**, **D**, **F**, **G** in $CHCl_3$ and object of a previous publication.[25]

The β_{CT} values obtained from these experiments are compared with CAM-B3LYP/6-31+G* data (Table 3). Notice that computed β_{CT} values are positively definited, according to what has already been reported in the literature.[26] Some discrepancies between extrapolated and CAM-B3LYP/6-31+G* data are noticed, mainly due to the different treatment of solvent effects in the two cases. In fact, estimated values refer to the Onsager solvent model (polarizable point dipole in a spherical cavity), whereas CAM-B3LYP/6-31+G* data are obtained with the QM PCM model, in which the solute is actually described with its wavefunction and is placed in a molecule-shaped cavity. However, in general a good agreement between extrapolated and DFT data is reported, thus confirming the quality of the experimental approach.

The results obtained from the EFISH experiments in term of $\mu_g \times \beta_{CT}$ can be then compared with the same quantity estimated in the present work through the solvatochromic method (see Table 4), with μ_g being in this case the ground state dipole moment value theoretically computed. The values estimated by the solvatochromic method are of the same order of magnitude than those directly measured by the EFISH technique. In the case of the thiophene derivatives **B**, **C** and **D** the agreement between the two values is really good; a certain overestimation by the solvatochromic method of the $\mu_g \times \beta_{CT}$ value is observed for the strongly push−pull systems **F** and **G** bearing the dibuthylamino donor. $\mu_g \times \beta_{CT}$ values obtained from solvatochromism are also in fair agreement with CAM-B3LYP/6-31+G(d) ones for the compounds **B** and **D**. Notice also that our DFT value for compound **B** is in good agreement with what has been recently reported in the literature.[26] To end the discussion on the calculated DFT $\mu_g \times \beta_{CT}$ data, it is worth pointing out that some discrepancies in the absolute values with respect to the EFISH experiment are predicted, and that is probably due to the choice of the level of theory adopted.

It has to be noted that the β value for compounds **B** and **C** has been derived by the solvatochromic method by referring to the oscillator strength and absorption maximum frequency in $CHCl_3$, the same solvent where the EFISH experiments for the five considered compounds were carried out, to allow a more proper direct comparison. In principle, EFISH is precluded in the case of ionic species due to ion migration phenomena, which might interfere with the experiment. For this reason, $CHCl_3$ was chosen as solvent for the EFISH experiments: the low polarity of the medium might stabilize undissociated ion pairs and thus allow avoiding ion migration. Also from our spectral data we could get some hints of the contribution to light absorption of ionic couples between the cationic chromophore and the iodide in $CHCl_3$. Given this fact, a slightly more polar solvent (DCM) was chosen in our solvatochromic procedure to measure the absorption coefficient, from which the oscillator strength and transition frequency were derived, for estimation through the Oudar equation of the non−linear optical properties of the cationic dyes. The different solvent considered, implying a different amount of ionic couples with respect to the dissociated cation responsible for the observed optical response, may thus give a possible explanation for the discrepancy in the $\mu_g \times \beta_{CT}$ values measured by EFISH and estimated by the solvatochromic method in the case of compounds **F** and **G**. Also, it has to be pointed out that the evaluation of equivalent radius according to the Onsager approximation of a spherical cavity used in our solvatochromic procedure works well for small, nearly spherical molecules but might be not very suitable in the case of elongated molecules such as **F** and **G**.[53] In any case, our findings constitute a solid validation of the capacity of the simple solvatochromic method to furnish an accurate estimation of the hyperpolarizability of small charged donor−acceptor chromophores in alternative to sophisticated direct spectroscopic investigations such as EFISH measurements. This ability of the solvatochromic method, previously shown in the case of neutral dipolar organic compounds characterized by a positively fluorosolvatochromic behavior,[21] is here demonstrated for cationic push−pull dyes exhibiting negative solvatochromism.

The results of the solvatochromic estimation of hyperpolarizability on cationic thiophene containing dyes (in terms of β_{CT} and β_0 values) reported in Table 3 allow interesting conclusions about the structural effect on the non−linear optical properties of these systems to be drawn. In particular, introduction of additional aromatics on the basic structure of a methylpyridinium−ethylene−thiophene skeleton ($\beta_0 = 14\times10^{-30}$ esu^{-1} cm^5 for **A**) results in an increased hyperpolarizability, either if a phenyl ($\beta_0 = 18$ and 33×10^{-30} esu^{-1} cm^5 for **B** and **C**, respectively) or a second thiophene ($\beta_0 = 29\times10^{-30}$ esu^{-1} cm^5 for **D**) are added. Also, replacing a methyl pyridinium with a methyl quinolinium implies an enhanced hyperpolarizability ($\beta_0 = 29$ and 37×10^{-30} esu^{-1} cm^5 for **D** and **E**, respectively). All these findings suggest that increased conjugation and molecular dimensionality has a positive impact on the non−linear optical response of these organic chromophores. When comparing the hyperpolarizability obtained in the case of compounds **B** and **C**, it is apparent that also the attach position of the additional phenyl with respect to the thiophene ring has a non−negligible influence on the resulting β values. It has to be noted that when a strong electron donor portion is introduced in the molecular structure, such as a dibuthyl amino group or a pyperidine, the latter largely improves (almost one order of magnitude enhancement) the non−linear optical properties (for instance $\beta_0 = 29$, 152 and 204×10^{-30} esu^{-1} cm^5 for **D**, **F** and **H**, respectively). This is related to the coupled effect of increased intramolecular charge transfer character of the absorption transition (higher $\Delta\mu$) and significant red shift of the absorption spectra position (lower υ_{eg}) in equation (3) for compounds **F**−**I**. Pyperidine as electron donor appears to be the most effective in inducing better non−linear optical properties and methyl quinolinium in replacement of methyl pyridinium as electron acceptor portion proves to give the highest hyperpolarizability ($\beta_0 = 439\times10^{-30}$ esu^{-1} cm^5 for **I**).

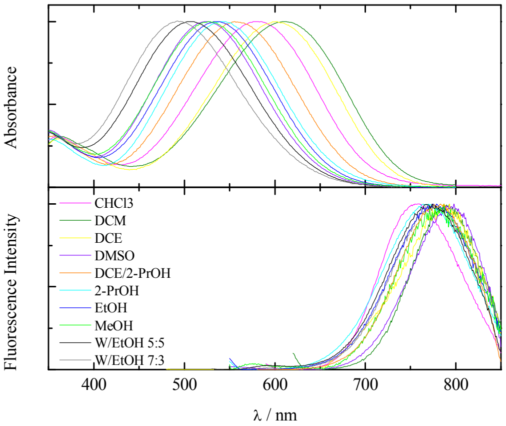

Figure 4. Normalized absorption and emission spectra of compound **H** in solvents of different polarity.

Table 2. Absorption and emission properties of compound **H** in solvents of different polarity (expressed as E_T^N parameter).

Solvent	E_T^N	λ_{abs} / nm	λ_{em} / nm	$\Delta\upsilon$/cm^{-1}	ε /M^{-1} cm^{-1}	ϕ_F
$CHCl_3$	0.259	581	757	4000		0.025
DCM	0.309	609	793	3810	33700	0.0032
DCE	0.327	600	793	4060		0.0074
DCE/PrOH 5:5	0.436	557	781	5150		
DMSO	*0.441*	*524*	*795*	*6505*		*0.0048*
2−PrOH	0.546	540	770	5530		0.023
EtOH	0.654	539	779	5720		0.0076
MeOH	0.762	527	787	6270		0.0016
W/EtOH 5:5	0.827	506	771	6790		
W/EtOH 7:3	0.896	492	777	7455		

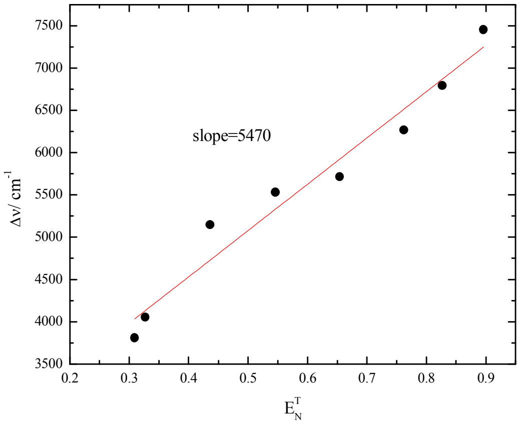

Figure 5. Plot of the Stokes shift (Δυ) as a function of the E_T^N parameter for compound **H**.

Table 3. Calculated parameters for compounds **A–I** (ground state dipole moment, μ_g; Frank−Condon excited state dipole moment, $\mu_{e,FC}$; Onsager cavity radius, a) and experimental parameters (frequency of the absorption maximum in DCM, υ_{eg}; oscillator strength, f; change of dipole moment, $\Delta\mu_{exp}$; extrapolated hyperpolarizability coefficient, β_{CT}, and β_0 in DCM) derived by their solvatochromism using equations (2) and (3). CAM-B3LYP/6-31+G* β_{CT} values ($\beta_{CT,calc}$) are also reported.

Comp.nd	μ_g /D	$\mu_{e,FC}$ / D	a /10^{-8} cm	slope	$\Delta\mu_{exp}$ /D	υ_{eg} /cm^{-1}	f	$\beta_{CT, calc}$ /10^{-30} esu^{-1} cm^5	β_{CT} /10^{-30} esu^{-1} cm^5	β_0 /10^{-30} esu^{-1} cm^5
A	6.21	3.72	7.29	2500	−5.40	24510	0.460	31	18	14
B	5.99	4.71	8.94	2320	−7.06	25000[a]	0.501[a]	59[a]	23[a]	18[a]
C	6.15	4.65	8.93	2320	−7.06	23200[a]	0.734[a]	29[a]	44[a]	33[a]
D	8.76	5.33	8.89	2650	−7.48	21880	0.492	76	39	29
E	7.24	5.04	10.16	2880	−9.53	19800	0.367	119	55	37

F	10.76	6.78	10.36	3920	−11.45	15150	0.568	274	332	152
G	8.97	7.53	11.43	2540	−10.68	13440	0.964	402	1041	345
H	13.93	8.67	11.42	5470	−15.65	16420	0.708	272	383	204
I	11.93	7.65	12.70	5295	−18.06	14225	0.861	417	1114	439

[a] in $CHCl_3$.

Table 4. Comparison between the $\mu_g\times\beta_{CT}$ values estimated through the solvatochromic method, calculated values and measured by EFISH experiments.

Compound	$\mu_g\times\beta_{CT}$ / 10^{-48} esu^{-1} cm^5		
	solvatochromic method	calculated CAM-B3LYP/6-31+G*	Experimental EFISH*
B	138	215	180
C	271	116	213
D	342	278	307
F	3570	1009	1240
G	9340	850	1250

*From ref. 25

Excited state dynamics

A deep insight into the excited state dynamics of the investigated cationic chromophores has been gained through femtosecond transient absorption measurements in various solvents of different polarity. The obtained results are presented in Figures where the upper panel (A) reports the three−dimensional matrix of data (ΔA vs. wavelength and time); the central panel (B) shows the time resolved absorption spectra and in the inset the kinetics recorded at meaningful wavelengths; the lower panel (C) contains the results of the Target Analysis of the acquired data in terms of lifetimes and Species Associated Spectra (SAS) of the components resulting from the Global Fitting procedure.

Figure 6 shows the femtosecond transient absorption data recorded in the case of compound **D** in MeOH as a representative example. The time resolved spectra exhibit a positive band of Excited State Absorption (ESA) peaked around 530 nm and a negative band due to Stimulated Emission (SE) centered at 620 nm. Decay kinetics were detected at wavelengths corresponding to the ESA signal and growth kinetics in the SE spectral region, which both get back to an almost zero differential absorbance signal within 100 ps. The Global Fitting of these data revealed the presence of three exponential components characterized by lifetimes of 0.22, 1.6 and 16 ps in addition to a Rest component, which does not decay within the investigated time window. The 400 nm excitation in the case of **D** in MeOH likely leads to the population of a vibrationally hot excited S_1 state (see Figure 1). The excited state dynamics following light absorption does not imply significant spectral changes (Figure 3) and might be thus rationalized considering the relaxation of one single electronic state (S_1). The first two components evidenced by the fitting (0.22 and 1.6 ps) may be attributed to the occurrence of inertial and diffusive solvation in MeOH,[54] possibly coupled with vibrational cooling. The 16 ps component exhibiting a SAS with a negative peak in the region of the steady state emission of **D** (see Figure 1) is assigned to its relaxed fluorescent S_1 state. The Rest component is likely due to the population of a long−lived excited triplet state (T_1), which might be efficiently produced for this thiophene containing dye. Investigation of the solvent effect on the excited state dynamics of compound **D** resulted in a similar behavior in all the considered media (see Table 5 and Table S7).

For all the thiophene derivatives **A**−**E** the acquired transient absorption spectra are dominated by positive signals of ESA and negative bands due to SE (see Figures S3, S6, S9 and S13 in the

Supporting Information). The excited state dynamics can be described in all cases as the relaxation of the fluorescent S_1 state followed by production of T_1 observed as a Rest component (Table 6), at least for the compounds richest in thiophenes among those under study. The lowest excited singlet state is characterized by a lifetime clearly enhanced upon increasing molecular conjugation. For instance τ_{S1} shows values of 12, 57 and 91 ps for compounds **A**, **D** and **E** in MeOH, respectively. The S_1 lifetime is thus lengthened when an additional thiophene is considered (when going from **A** to **D**) or when the methyl pyridinium is replaced by a methyl quinolinium (when passing from **D** to **E**). It has to be noted that a decrease of the S_1 state lifetime with the solvent polarity has been observed for all the compounds **A**−**E** (see the results obtained in the low polar DCM and in the polar MeOH solvent in Table 5). This finding suggests a certain intramolecular charge transfer character of this state, with this behavior being quite usual for push−pull systems such as those under investigation.[12−14] A more complete investigation of the effect of the solvent polarity on the excited singlet lifetime for compounds **A**−**E** is reported in the Supporting Information (see Tables S2, S7 and S9).

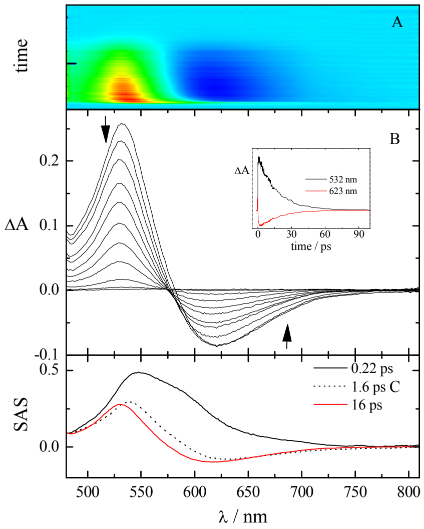

Figure 6. Pump−probe absorption spectroscopy of **D** in MeOH (λ_{exc} = 400 nm): (A) Contour plot of the experimental data, (B) time−resolved absorption spectra recorded at different delays after the laser pulse (inset: decay kinetics recorded at meaningful wavelengths) and (C) species associated spectra obtained by target analysis.

Table 5. Excited state lifetimes of compounds **A**−**E** in two solvents of different polarity (obtained by femtosecond transient absorption measurements upon excitation at 400 nm).

Solvent	τ / ps					Transient
	A*	**B**	**C**	**D**	**E**	
DCM	0.11	1.0	0.13	0.37	0.29	Solv.
			0.42			Solv.
	3.4	3.3	3.7	8.2	15	VC
	12	59	14	57	91	S_1
	Rest	Rest	Rest	Rest	Rest	T_1
MeOH	0.52	0.14	0.22	0.22	0.20	Solv.
		2.0	1.0	1.6	1.6	Solv.
					6.9	Solv.
	5.3	14	5.2	16	70	S_1
	Rest			Rest	Rest	T_1

*$CHCl_3$ and Water

In Figure 7 the results of the ultrafast transient absorption investigation in the case of **G**, **H** and **I** in DCM are reported. Data relative to the other methyl pyridinium derivative exhibiting a strong electron donor group, that is the dibuthyl–amino group (compound **F**) were the object of a previous publication from our research group.[16] The time resolved spectra show a ESA peak around 580–600 nm; a negative band due to ground state bleaching (GSB) centered at 750 nm (for **G**), 650 nm (for **H**) and 700 nm (for **I**); a SE signal above 800 nm for **G** and **I** and around

800 nm for **H**. The global fitting of these data revealed the presence of three transient species (Table 6 and 7): the first two may be attributed to solvation dynamics and vibrational cooling for the excited chromophores in DCM;[54] the third to the decay of the lowest excited singlet state (S_1). This state exhibits a lifetime of ca. 100 ps for the methyl pyridinium derivatives in DCM (**F** and **H**) and of ca. 20 ps for the methyl quinolinium derivatives in this low polar solvent (**G** and **I**). The SAS of this state is characterized for all the four chromophores by the intense ESA band peaked before 600 nm and in the case of the two pyperidine derivatives by the hint of a second positive absorption signal around 700 and 800 nm for **H** and **I**, respectively.

In the transient spectra recorded in MeOH (see Figure 8) the presence of this second ESA band becomes apparent around 770 nm (**G**), 670 nm (**H**) and 730 nm (**I**), as it was unambiguously evidenced during the previous ultrafast investigation of compound **F** in the same solvent.[16] The global fitting of this matrices of data (see Table 6) evidenced besides the solvent relaxation components a shorter living S_1 state transient (with respect to that revealed in DCM), whose SAS (red line in panel C of Figure 8) is characterized by the clear absorption contribution of two ESA bands in the case of **G** and **H**, as it was previously reported for compound **F**. A different behavior was found for **I** in the polar MeOH solvent, where the two absorption bands are associated to two distinct lifetimes of 4.3 and 7.2 ps (Table 7). The bathochromic ESA band likely corresponds to the contribution of an intramolecular charge transfer (ICT) excited state, which results mixed to the locally excited (LE) state reached by photoexcitation for the push−pull systems **F**, **G** and **H** in a polar solvent (MeOH). This ICT excited state is observed as a separate state in the case of **I** in MeOH, with this dye being the one among those under investigation bearing the strongest electron donor (pyperidine) and electron acceptor (methyl quinolinium) portions.

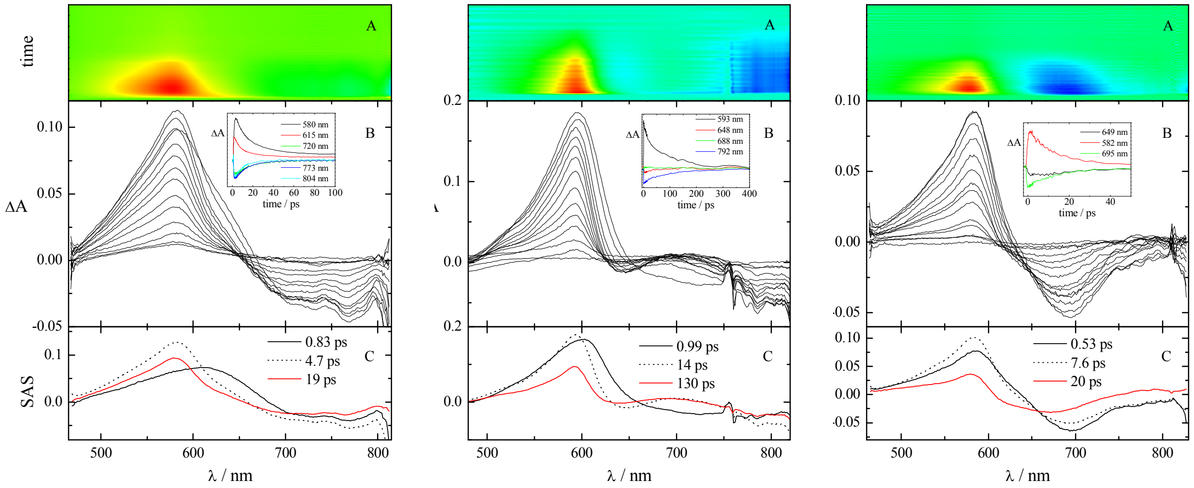

Figure 7. Pump−probe absorption spectroscopy of **G**, **H** and **I** in DCM (λ_{exc} = 400 nm): (A) Contour plot of the experimental data, (B) time−resolved absorption spectra recorded at different delays after the laser pulse (inset: decay kinetics recorded at meaningful wavelengths) and (C) species associated spectra obtained by target analysis.

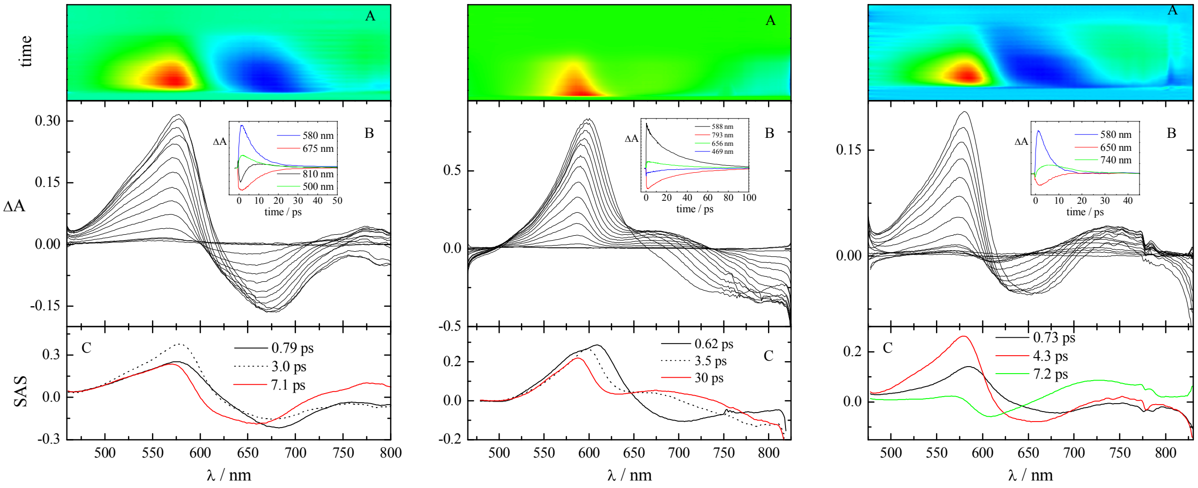

Figure 8. Pump−probe absorption spectroscopy of **G**, **H** and **I** in MeOH (λ_{exc} = 400 nm): (A) Contour plot of the experimental data, (B) time−resolved absorption spectra recorded at different

delays after the laser pulse (inset: decay kinetics recorded at meaningful wavelengths) and (C) species associated spectra obtained by target analysis.

Table 6. Excited state lifetimes of compounds **F**−**H** in two solvents of different polarity (obtained by femtosecond transient absorption measurements upon excitation at 400 nm).

Solvent	τ / ps			Transient
	F[*]	**G**	**H**	
DCM	0.17	0.83	0.99	Solv.
	2.5	4.7	14	Solv./VC
	90	19	130	S_1 (LE)
MeOH	0.22	0.79	0.62	Solv.
	1.0	3.0	3.5	Solv.
	5.1			Solv.
	41	7.1	30	S_1 (LE/ICT)

[*] from ref. 16

Table 7 . Excited state lifetimes of compound **I** in two solvents of different polarity (obtained by femtosecond transient absorption measurements upon excitation at 400 nm).

Solvent	τ / ps	Transient
	I	
DCM	0.55	Solv.
	7.6	Solv.+VC
	20	S_1 (LE/ICT)
MeOH	0.73	Solv.
	4.3	Solv.+S_1 (LE)
	7.2	S_1 (ICT)

Conclusions

This study represents a successful attempt to develop a reliable procedure in order to use the solvatochromic method to estimate the hyperpolarizability of cationic push–pull chromophores. The case study are nine dipolar donor–π–acceptor derivatives where the electron acceptors are the positively charged methyl pyridinium or quinolinium and the electron donors are electron rich thiophene rings eventually coupled with the strongly electron donating dibuthylamino group or pyperidine. All these chromophores have shown a significant blue shift of their absorption spectra upon increasing the solvent polarity (the rarely reported negative solvatochromism) and a negligible solvent effect on the emission band. This solvatochromic behavior has been comprehended considering the results of the quantum mechanical calculations, which predict a decrease of the dipole moment upon photoexcitation. The solvatochromic shifts have been rationalized according to the Reichardt theory considering the E_T^N solvent polarity parameter to obtain information from the experimental data about the difference between the excited and ground state dipole moment (Δμ). The frequency dependent and static hyperpolarizability (β) were computed through the Oudar equation. The μ×β values obtained from the present investigation could be directly compared, in some cases, with those retrieved by EFISH measurements of the same compounds in the low polar $CHCl_3$ solvent and also with those calculated through a quantum mechanical approach based on the density functional theory and the polarizable continuum model. These values were found to be in total agreement. This result thus constitutes a solid validation of the ability of the simple solvatochromic method here employed to furnish an accurate estimation of the β value. Moreover, this method could be used by referring the computations not only to such a low polar solvent where the cationic chromophore is probably engaged in an ionic couple with the iodide counterion, but also in solvents of higher polarity where the cation itself is indeed responsible for the observed optical response. This is surely an added value of the solvatochromic method: in fact isolated charged species cannot be investigated by EFISH because of ion migration effects, which can interfere with the experiment.

The large number of compounds under study allowed interesting structural effect on the hyperpolarizability to be investigated. It was clearly observed that an increase in molecular dimensionality and conjugation has a positive impact on the non−linear optical (NLO) properties of these chromophores. The higher β values are associated with the chromophores bearing the stronger electron donor groups (such as dibuthyl amino and pyperidine). In particular, the best response is observed (β_0=439×10^{-30} esu^{-1} cm^{5}) for the system bearing a methylquinolium as electron acceptor and a pyperidine coupled with a bithienyl as electron donor (compound **I**). Very interestingly, this compound has shown a peculiar excited state dynamics among all the others during the femtosecond transient absorption investigation. In fact, the ultrafast study evidenced for all the dipolar systems the mere relaxation (vibrational cooling and solvent relaxation) of a single electronic state (S_1), the one reached by light absorption, followed in some cases by the population of the lowest excited triplet state (T_1). In the case of compound **I** in a polar solvent, a second distinct excited singlet transient has been detected, produced upon decay of the locally excited singlet state and attributed to the formation of an intramolecular charge transfer (ICT) state. Production of the ICT state as a separate species is thus observed only in the case of the compound bearing the strongest electron donor and electron acceptor groups, the same compound for which the highest hyperpolarizability has been found. This finding suggests that a factor significantly affecting the NLO response of organic materials is the efficiency of the photoinduced ICT taking place in these molecules. The important NLO capacities of the best performing chromophores combined with their therapeutic properties as potential antitumor agents[17,18] make them particularly appealing as molecular markers to localize and characterize their biological sites of interaction through NLO imaging techniques.

ASSOCIATED CONTENT

Supporting Information. Supporting information contains results about absorption and emission spectra and femtosecond transient absorption data in solvents of different polarity for all the compounds not shown in the main paper.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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