A 'donor-free' chromophore with a silicon-based acceptor group for second order nonlinear optics

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Abstract

In this paper we report an investigation on the linear and nonlinear properties of a non-classic push-pull molecule, based on the molecular design concept of a ‘donor-free’ chromophore. Herein a terthiophene unit acts both as a donor and a π-spacer group and a tris(trimethylsiloxy)silane substituent as an acceptor group. This latter can represent a model of a fragment of silica surface and it has been compared with a classic acceptor unit like the nitro group. The ‘donor-free’ chromophores have also been compared to ~~a~~ more typical push-pull chromophores by replacing the terthiophene unit with the N,N-dimethylamino donor group.

Despite the silane group only slightly impacts on the electronic and linear properties of the terthiophene, our results reveal high $\mu\beta_{EFISH}$ values for silane-functionalized derivatives producing a NLO activity stronger than that of the nitro substituted. Finally, ~~T~~the investigated ‘donor-free’ NLO-phore exhibits interesting physical properties relevant in term of nonlinearity/transparency trade-off, a highly desired requirement for second-order NLO materials.

keywords

second-order nonlinear optics, terthiophene, siloxane, ‘donor-free’ NLO-phore

1. Introduction

After the discovery of laser sources at the beginning of 60s, nonlinear optics (NLO) has been rapidly developed and today impacts on some day-life laser applications, ranging from laser technologies (generation of new colours, modification of pulses, spatial and frequency control), to permanent or transient modification of materials (machining, spectroscopy and analysis tools like imaging processes *in vitro* and *in vivo*) and to information technologies (telecommunications, data storage and sensors).[1]

Indeed, NLO phenomena can be observed when the strong oscillating electromagnetic field associated to the laser beam interacts with a material~~,~~ : ~~it~~ this produces a perturbation on the electrons of the material inducing a nonlinear polarization and thus a modification of its electronic and optical properties.

Among these optical properties, the second harmonic generation (SHG) has attracted much interest producing the effect of doubling the frequency of the incident light, thus generating a new colour emission, *i.e.* from a near-infrared (NIR) light source, for example, it is possible to obtain a light emission in the visible range.

Organic molecules having extended π-delocalized structure, rich of electrons and therefore highly polarizable, are ideal materials for SHG. However other requirements are necessary to obtain a chromophore with secondo-order NLO activity according to the Oudar theory: a non-centrosymmetric charge distribution; one or more excited states energetically close to the ground state with a corresponding significant charge transfer (CT); a significant difference between the dipole moment of the excited state and the one of the ground state.[2,3]

The so-called ‘push-pull’ molecules, where an electron donor group (D) and an electron acceptor group (A) are linked by a π-conjugated bridge, largely satisfy all these requirements.[4,5]

During the past decades a lot of work have been done to design and synthesis new and even more efficient molecules with improved second-order NLO activity.[6,7]

Beside the classic push-pull systems with an amino donor (D) and a nitro acceptor group (A), various molecular architectures have been developed and studied over the years through different approaches, also including metal complexes[8] and organometallic compounds.[9]

For example, systems with a more elaborate molecular skeleton of the π bridge have been proposed to increase the conjugation between donor and acceptor groups and consequently the internal charge transfer process (ICT).[10–16] In other cases, on the one hand, the classical acceptor groups (-NO_2, CN, etc.) have been replaced with molecular fragments which, by exploiting resonance mechanisms, give rise to a better charge separation.[11] On the other hand, aliphatic amines (donor groups initially used) have been substituted with triarylamines, richer of polarizable electrons and therefore more efficient in the electron density donation process. ~~Then~~Finally, ~~when~~ by developing of molecules with a net charge separation already present at their ground state such as the π-conjugated zwitterions, the ~~principle~~ concept of push-pull molecule ~~is~~ has been leaded to the extreme and ~~in a net charge separation already present in the starting molecule like in the π-conjugated zwitterions,~~ exceptional high values of SHG ~~can be~~have been measured.[17]

Nevertheless, ~~O~~other approaches have been developed~~studied~~ to improve the SHG response consisting in the pre-organization of NLO-chromophores on an organic[18,19] or inorganic[20] scaffold: the pre-alignment in a ‘parallel arrangement’ of the chromophore units allow to maintain a non-centrosymmetric system and at the same to ~~sum~~ add the contributes of each unit. More recently, also a ‘series arrangement’ with two donor fragments linked together, according to the donor-donor-acceptor (DDA) scheme, was investigated and lead to an increase in the nonlinear optical properties of the second order compared to the corresponding molecular systems DA.[21]

The experience acquired on molecular structures characterized by strong charge transfer, such as push-pull molecules for NLO, has allowed the scientific community to develop other research sectors rapidly and extensively, such as third-generation organic photovoltaics. In particular, Dye-Sensitized Solar Cells (DSSCs), introduced and developed by Grätzel in the early 1990s,[22] enormously ~~benefited~~ took advantage of~~from~~ this basic knowledge, in fact the best dyes for this kind of devices are push-pull systems.[23]

Recently, in this context, a new kind of dye ~~has been reported,~~ characterized by the presence of a fragment of conducting polymer, *i.e.* a pentathiophene unit, functionalized with a single anchoring/acceptor group, has been reported~~which has~~ to show~~n~~ photoconversion efficiencies comparable to an analogous chromophore equipped with a terminal carbazole unit as a donor in a typical push-pull molecular configuration.[24] By lacking the donating group, this chromophore was proposed as an example of ‘donor-free’ dye.[24] The experimental data indicate that the efficiency of this dye is ascribed to a better delocalization of the "hole", namely the positive charge formed as a result of the photoexcitation process and the consequent charge injection into the semiconductor.[24] To date there are few works on this topic, but they have shown how these systems, based on polythiophenic fragments, can actually represent a very interesting new class of dyes.[25–27] In the perspective of large-scale applications they would simplify the synthetic procedures making the presence of aromatic amines unnecessary. The latter, indeed, are today well-recognized as carcinogenic and harmful substances for the environment.

However, it remains to clarify whether this polythiophenic fragment should actually be considered a donating group in a non-classic push-pull system.

~~Being~~ Since the molecular design of the dyes and their charge transfer processes are in common with both solar cells and NLO-application, we decided to ~~prompted us to~~ ~~study~~ investigate whether this new class of 'donor-free' chromophores, lacking amino-based donating groups, ~~shows~~ has push-pull character and, therefore, shows second-order NLO activity.

Polythiophenic systems have already been studied from the point of view of non-linear optics, but they have always been used as π-conjugated spacers, due to the electron-rich character of thiophene ring offering a better polarization than the benzene ring, when a donor and an acceptor group are linked to the opposite ends of the molecule.[18,28–32] Thiophenic polymers are also known to show third-order NLO properties by giving rise to centrosymmetric bulk materials.[33] In a very few cases they have been used as a donor group within a push-pull molecule, as either a phosphine ligand in Pd and Pt complexes,[34,35] or linked to a carborane unit.[36]

The aim of this work, therefore, was to verify and study the NLO properties of an analogous ‘donor-free’ system, based on a rather simple molecular design with a terthiophene unit bearing a silicon-based acceptor group, namely $-Si(OSiMe_3)_3$. This latter can represent a simplified model of a fragment of silica surface,[20] previously studied in our laboratory from photophysical point of view (see Figure 1).[37]

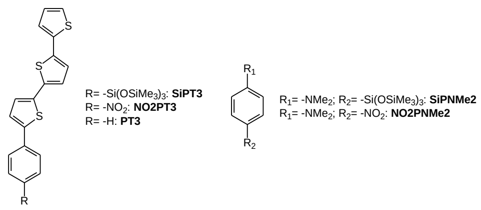

Figure 1. Molecules investigated.

For a more comprehensive study a series of benzene-based compounds with either siloxane or $-NO_2$ acceptor groups and with N,N-dimethylamine donor group (**SiPNMe2** and **NO2PNMe2**) were prepared and compared with the pristine terthiophene (**PT3**) and its derivatives with either silicon- (**SiPT3**) or NO_2-acceptor (**NO2PT3**, Figure 1).

The interest in this silicon-based substituent systems comes from our previous ~~study~~studies, where it has been used as an active component in the molecular design, providing ~~the~~ push-pull systems with unexpected NLO activities. In fact, from the comparison between the experimental data relating to chromophores having the same structure in terms of donor group and π-conjugated spacer, but bearing a group $-Si(OSiMe_3)_3$ or $-NO_2$ as acceptor, the silicon-based substituent behaves as a strong acceptor group comparable to the $-NO_2$ from the point of view of the second-order NLO properties.[20] This unexpected pull character of the –Si(OSiMe$_3$)$_3$ fragment had therefore been ascribed to a probable charge redistribution on the population of the excited-state involved in the charge transfer process, and favored by the empty *d* orbitals of the silicon or by the σ* orbitals on the Si-based group.[20,38]

2. Material and methods

2.1 General

All reagents and solvents used in the synthesis were purchased by Sigma Aldrich and used as received, except THF (freshly distilled from Na/benzophenone). Silica gel for gravimetric chromatography (Geduran Si 60, 63-200 μm) and for flash chromatography (Geduran Si 60, 40-63 μm) were purchased by Merck. Glassware has been flame-dried under vacuum before use when necessary.

Compound **SiPT3** and **PT3** were synthesized as previuosly reported in literature.[37]

^{1}H NMR spectra were recorded on a Bruker Avance DRX-400 in CDCl$_3$ or CD$_2$Cl$_2$ as solvent (Cambridge Isotope Laboratories, Inc.).

Elemental analyses were carried out with a Perkin-Elmer CHN 2400 instrument in the Analytical Laboratories of the Department of Chemistry at the University of Milan.

Mass spectra were obtained by using a Thermo-Finnigan apparatus with an ion trap analyzer (positive mode) and an electrospray ionization source (ESI) using an LCQ Advantage instrument.

2.2 Absorption and emission spectroscopy

Electronic absorption spectra of porphyrin dyes in solution were recorded at room temperature in toluene, using a Shimadzu UV3600 spectrophotometer and quartz cuvettes with 1 cm optical path length Electronic absorption spectra were recorded using a Jasco V-530 spectrometer.

Photoluminescence experiments were carried out at room temperature, in THF solution after N$_2$ bubbling for 60 s.

Photoluminescence quantum yields were measured with a C11347 Quantaurus - QY Absolute Photoluminescence Quantum Yield Spectrometer (Hamamatsu Photonics K.K), equipped with a 150 W Xenon lamp, an integrating sphere and a multi-channel detector.

Steady state emission and excitation spectra and photoluminescence lifetimes were obtained with a FLS 980 spectrofluorimeter (Edinburg Instrument Ltd.). Continuous excitation for the steady state measurements was provided by a 450 W Xenon arc lamp. Photoluminescence lifetime measurements were performed using an Edinburgh Picosecond Pulsed Diode Laser EPL-445 (Edinburg Instrument

Ltd.), with central wavelength 442.2 nm and repetition rates 20 MHz, by time-correlated single-photon counting method.

2.3 Electrochemical measurements

The voltammetric studies have been performed in a 4 cm^3 cell, in 5×10^{-4} - 10^{-3} M solutions in CH_2Cl_2 (Aldrich) with 0.1 M tetrabutylammonium perchlorate (TBAP, Fluka) as the supporting electrolyte. The solutions were de-aerated by N_2 bubbling. The ohmic drop has been compensated by the positive feedback technique.[39]

The experiments were carried out using an AUTOLAB PGSTAT potentiostat (EcoChemie, The Netherlands) run by a PC with GPES software. Cyclic voltammetry (CV) investigations were carried out at scan rates typically ranging 0.05 to 2 Vs^{-1}, with ohmic drop compensation; differential pulse voltammetry (DPV) curves (step potential: 5 mV, modulation amplitude: 50 mV) were also recorded for each compound as both oxidative and reductive scans.

Differential pulse voltammetry (DPV) experiments have been carried out on the same solutions used for CV, solutions in order to better identify the $E_{p,Ia}$ and $E_{p,Ic}$, affording the calculation of $E^{0'}_{Ia}$ and $E^{0'}_{Ic}$ by the following equations:

$E^{0'}_{Ia} = E_{p,Ia} + \Delta E/2$

$E^{0'}_{Ic} = E_{p,Ic} - \Delta E/2$

where ΔE is the modulation amplitude.

The working electrode was a glassy carbon one (AMEL, diameter = 1.5 mm) cleaned by synthetic diamond powder (Aldrich, diameter = 1 μm) on a wet cloth (STRUERS DP-NAP); the counter electrode was a platinum disk or wire. The operating reference electrode was an aqueous saturated calomel electrode, but the potentials were ultimately referred to the Fc^+/Fc (ferrocinium/ferrocene) couple (the intersolvental redox potential reference currently recommended by IUPAC[40,41] by both external and internal standardization). To prevent water and chloride leakage into the working solution a compartment filled with the operating medium and ending with a porous frit was interposed between the reference electrode and the cell.

2.4 EFISH measurements

The molecular quadratic hyperpolarizabilities have been measured in CH_2Cl_2 and DMF solutions at 10^{-3}-10^{-4} M concentration by the Electric Field Induced Second Harmonic (EFISH) generation technique,[42] which provides direct information on the intrinsic molecular NLO properties through equation (1):

$$\gamma_{EFISH} = (\mu\beta_{\lambda}\,(-2\omega; \omega, \omega)/5kT) + \gamma\,(-2\omega; \omega, \omega, 0) \qquad (1)$$

where $\mu\beta_\lambda(-2\omega; \omega, \omega)/5kT$ represents the dipolar orientational contribution to γ_{EFISH} and γ (-2ω; ω, ω, 0), a third order term at frequency ω of the incident wavelength, is the electronic contribution to γ_{EFISH}, which is negligible for the kind of molecules here investigated.[43,44]

β_λ is the projection, working with an incident wavelength λ, along the dipole moment axis of the vectorial component β_{VEC} of the tensor of the quadratic hyperpolarizability.

All EFISH measurements were carried out working with a non-resonant incident wavelength of 1.907 μm, using a Q-switched, mode-locked Nd^{3+}:YAG laser manufactured by Atalaser equipped with a Raman shifter, while the apparatus for the EFISH measurements was made by SOPRA (Paris, France).

The uncertainty of the measure is about ± 15%. All the experimental EFISH $\beta_{1.907}$ values are defined according to the "phenomenological" convention.[45]

2.5 Solvatochromic measurements

The quadratic hyperpolarizability along the charge transfer direction, β_{CT}, has been determined by the solvatochromic method, taking into account the solvatochromic shift of the ICT absorption band in solvents of different polarity (toluene, *n*-hexane, ethyl acetate, THF, dichloromethane, chloroform, CCl_4, acetone, CH_3CN).[46]

According to the "two-level" model developed by Oudar [2,3], β_{CT} can be obtained by equation 2:

$$\beta_{CT} = \frac{3}{2h^2c^2}\frac{\nu_a{}^2 r_{eg}{}^2 \Delta\mu_{eg}}{(\nu_a{}^2 - \nu_L{}^2)(\nu_a{}^2 - 4\nu_L{}^2)} \tag{2}$$

where r_{eg} is the transition dipole moment related to the oscillator strength *f* of the absorption band by the equation: $r_{eg}^2 = 2.13 \times 10^{-30} f/\nu_{eg}$, ν_a is the frequency of the ICT absorption band, ν_L is the frequency of the fundamental incident radiation and $\Delta\mu_{eg}$ is the variation of the dipole moment between the excited and the ground state.

It is important to underline that EFISH derived β_λ and solvatochromic β_{CT} can be safely compared only when the direction of the dipole moment and that of the charge-transfer are almost coincident, as it occurs for the linear push-pull structures under investigation.

2.6 Dipole moment measurements

The ground state molecular dipole moment of **SiPT3** has been measured in $CHCl_3$ solution (99.9% HPLC grade, purchased from Sigma Aldrich) by the Guggenheim method.[47,48] We prepared five solutions with solute weight fraction values ranging from 4×10^{-4} to 3×10^{-3}, determined for solute and solvent weighing on analytical balance. Determination of the dielectric constant was carried out by measuring the capacity C, performed with a WTW model DM01 dipolmeter, equipped with a DFL 2 type measuring cell. The sensitivity of the instrument for the purpose of determining the dielectric constant ε, (expressed as Δε/ε) is equal to 10^{-5} at the frequency of 2.0 MHz. The measuring cell was kept at a constant temperature (25 °C) during the experiments by means of a thermostat. For each solution the measurement of the capacity value C was carried out after a period of 15 minutes at constant temperature. There is a linear relationship between the value of C thus determined and ε: $\varepsilon = a + bC$, where the values of a and b depend on the particular reading scale used for the measurement. To determine a and b, each experiment was preceded by the determination of the capacitance values for three pure solvents having known dielectric constant values and included in the reading range of the scale subsequently used for the measurements on the solutions. In particular, the reference solvents used were $CHCl_3$ (the same used later for the preparation of the solutions), C_6H_5Cl and AcOEt (at 25 °C, respectively, ε= 4.72, 5.621, 6.02). The corresponding capacitance values were used each time to construct the instrument calibration line, from which to obtain the coefficients a and b necessary for the calculation of ε starting from the capacitance values subsequently measured for the solutions. The refractive indices of the solutions were determined using a MISCO digital refractometer, at the constant temperature of 25 °C and using the pure solvent as a reference.

On the other hand, due to its low solubility in $CHCl_3$, the ground state molecular dipole moment of **NO2PT3** has been computed by computational method (see next paragraph).

2.7 Computational method

The molecular structure and properties of **NO2PT3** have been determined by quantum chemical calculations carried out at different level of theory. We have proved that a reliable prediction of the molecular dipole moments can be obtained only by using with a very flexible basis sets, including a variety of polarization functions. In particular, we have proved that methods like semi-empirical AM1,[49] DFT (BP86[50,51]/TZVP basis set[52]) give satisfactory results. We found, on the contrary, that a DFT approach using the B3LYP functional[53–56] and a flexible basis set including several polarization function cc-pVTZ[57] give very satisfactory results. The accuracy of the latter method has been tested on a set of small molecules like NH_3, CH_3F, CH_3Cl, H_2O, HCN, CH_3NO_2, LiF and LiCl, for which experimental data of the dipole moments are known.[58] These data cover the broad range 1.47-7.13D. Using the most accurate approach we tested (B3LYP/cc-pVTZ) we obtained the following regression line: $\mu_{exp} = 1.0672\mu_{calc} - 0.1943$, $R^2 = 0.9993$.

This proves that the B3LYP/cc-pVTZ approach is characterized by an accuracy sufficiently high to be used as a predictive tool, without support from experiments. This is particularly important in the context of the molecule investigated in the present paper: in fact, due to severe experimental difficulties, we could not obtain reliable experimental value of the dipole moment in chloroform solution. This suggested us to repeat theoretical calculations of the dipole moments also using the Polarizable Continuum Model (PCM)[59,60], mimicking a chloroform solution (dielectric constant = 4.8069 ε_0). The PCM value of dipole moment has been obtained in the best molecular geometry obtained by corresponding geometry optimization *in vacuo*.

2.8 Single crystal X-ray crystallographic studies

Single-crystal X-ray diffraction data for compound **SiPT3** were collected at 150 K on a Bruker APEX II CCD area detector diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). After integration, an empirical absorption correction was made on the basis of the symmetry-equivalent reflection intensities measured.[61]

The structures were solved by direct methods using SHELXS-97[62] and refined by full-matrix least-squares on F^2 by SHELXL-2018/3[63] using all reflections. Weights were assigned to individual observations according to the formula $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; a and b were chosen to give a flat analysis of variance in terms of F_o^2. Anisotropic parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were placed in idealized position and refined riding on their parent atom with an isotropic displacement parameter 1.2 (or 1.5) times that of the pertinent parent atom. The final difference electron density map showed no features of chemical significance, with the largest peaks lying close to the center of bonds.

Details relating to the crystals and the structural refinements are presented in Table 1. Full details of crystal data and structure refinement, in CIF format, are available as Supplementary Information. CCDC reference number: 2097658.

Table 1. Crystal data, data collection and refinement details for compound **SiPT3**

	SiPT3
Crystal data	
Chemical formula	$C_{27}H_{38}O_3S_3Si_4$
M_r	619.11
Crystal system	triclinic
Space group	P-1
Temperature [K]	150(2)
a [Å]	6.5518(4)
b [Å]	19.6684(12)
c [Å]	26.0876(16)
α [°]	81.9139(7)
β [°]	89.3043(7)
γ [°]	81.3414(7)
V [$Å^3$]	3290.2(3)
Z	4
μ(MoKα) [mm^{-1}]	0.397
Crystal size [mm]	0.42 × 0.32 × 0.15
Data collection	
T_{min}, T_{max}	0.951, 0.998
No. of measured reflections	15292
No. of observed reflections [$I > 2\sigma(I)$]	11429
R_{int}	0.0291
R_σ	0.0362
$(\sin \theta/\lambda)_{max}$ [$Å^{-1}$]	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$	0.0418
$wR(F^2)$	0.1078
S	1.037
No. of reflections	15292
No. of parameters	685
No. of restraints	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.724, –0.698

3. Experimental

3.1 Synthesis of NO2PT3

In a dry Schlenk tube 144.1 mg (0.7133 mmol) of 1-bromo-4-nitrobenzene and 525.9 mg (1.405 mmol) of 2,2':5',2''-terthiophene-5-boronic acid pinacol ester were dissolved in 6 mL of THF and the solution was de-aerated at -78 °C by three freeze-pump-thaw cycles. The solution was allowed to reach room temperature, then a solution of 41.2 mg of [Pd(PPh$_3$)$_4$] (35.7 μmol, 5% mol) in 3 mL of THF and 3 mL of K_2CO_3 1 M aqueous solution, previously de-areated, were added under N_2 atmosphere. The reaction mixture was heated under vigorous stirring at 70 °C for 24 h. The final mixture was allowed to cool to room temperature, transferred in a separatory funnel and extracted from CH_2Cl_2. The organic phase was neutralized by aqueous HCl 1 N and then washed with brine and dried over anhydrous $MgSO_4$. Then the solvent was removed *in vacuo*. The residue obtained was purified by flash column chromatography (silica gel, *n*-hexane/CH_2Cl_2 7:3, R_f: 0.23) to afford 91.8 mg (34.8% yield) of pure product as a yellow solid. ^{1}H NMR (CD_2Cl_2), δ, ppm: 8.27 (d, 1H), 7.79 (d, 1H), 7.50 (d, 1H), 7.31 (d, 2H), 7.28 (d, 3H), 7.25 (d, 1H), 7.19 (d, 1H), 7.09 (m, 1H); MS-ESI$^+$: *m/z*: 370.6 $[M+H]^+$; elemental analysis calcd (%) for $C_{18}H_{11}NO_2S_3$: C 58.51, H 3.00, N 3.79; found C 58.32, H 3.03, N 3.76.

3.2 Synthesis of SiPNMe2

765.3 mg of 4-bromo-N,N-dimethylaniline (3.825 mmol) were placed in a dry 250-mL 3-necked flask and de-aerated with three vacuum-nitrogen cycles. The reagent was dissolved with 100 mL of anhydrous Et_2O and the solution obtained was cooled to 0 °C. Under stirring, 3.6 mL of 1.6 M *n*-BuLi in hexane (5.76 mmol) were added drop by drop. When the addition was complete, the mixture was allowed to react for 3 hours at 0 °C. Then at 0 °C, 2.8 mL of $ClSi(OSiMe_3)_3$ (7.8 mmol) were added. A white precipitate (LiCl) was formed and the reaction was allowed to warm to room temperature overnight under continuous stirring. The solvent was removed *in vacuo* and the residue obtained was extracted with 200 mL of *n*-hexane and 100 mL of CH_2Cl_2 and then filtered on celite. The solvent was removed and the crude product was purified by column chromatography (silica gel, AcOEt/*n*-hexane 0.5:9.5, R_f = 0.60). 796.0 mg of product were obtained (50.05% yield). ^{1}H NMR ($CDCl_3$), δ, ppm: 7.44 (d, 2H), 6.72 (d, 2H), 2.99 (s, 6H), 0.13 (s, 27H); MS-ESI$^+$: *m/z*: 416.4 $[M+H]^+$; elemental analysis calcd (%) for $C_{17}H_{37}NO_3Si_4$: C 49.10, H 8.97, N 3.37; found C 48.97, H 8.99, N 3.36.

4. Results and discussion

4.1 Synthesis

The compound **SiPT3** can be easily obtained by a direct Suzuki coupling reaction between the commercial available 2,2':5',2''-terthiophene-5-boronic acid pinacol ester and the 4-bromophenyl-tris(trimethylsiloxy)silane in good yield (65%[37]). Though with lower yields, the other chromophores containing the terthiophene unit can be obtained with the same synthetic method (34.8% and 24%[37] respectively for **NO2SiPT3** and **PT3**). The lowest reaction yield observed for **PT3** should be not underestimated, indeed -Si(OSiMe$_3$)$_3$ group, due to its considerable steric hindrance (see after), makes very soluble the intermediates in the most common organic solvents by preventing aggregation forms and thus favoring the reactions progress.

SiPNMe2 (and 4-bromophenyl-tris(trimethylsiloxy)silane) has been prepared from the corresponding carbanions, obtained by treatment of the starting reagents with *n*-butyllithium, and tris(trimethylsiloxy)chlorosilane in 50% yield.

4.2 Absorption and emission spectroscopy characterization

The electronic features of **SiPT3** were firstly compared with the ones of **NO2PT3**. The impact of the –Si(OSiMe$_3$)$_3$ group on energy levels and on spectroscopic, electronic and optical properties of terthiophene unit, when compared to those obtained with –NO$_2$ group, represents the main focus of this work.

Therefore, the absorption and emission spectra of **SiPT3** and **NO2PT3** were recorded under the same conditions in CH$_2$Cl$_2$ solution at 10^{-5} M concentration (see Figure 2).

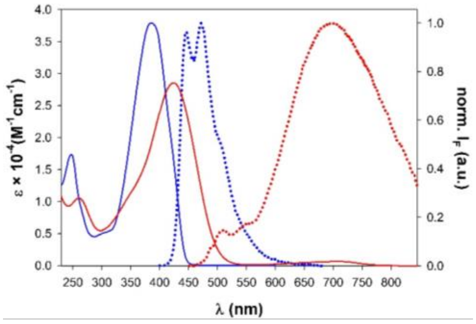

Figure 2. Absorption (solid line) and emission (dotted line, λ_{exc} = 386 nm) spectra of **SiPT3** (—) and **NO2PT3** (—) in CH$_2$Cl$_2$.

The absorption spectra are characterized by a rather intense and unstructured band at 386 nm for **SiPT3** and at 423 nm for **NO2PT3**~~. ~~, which~~The unstructured shape~~ can be attributed to a π → π* transition~~,~~. This absorption band ~~which~~ is clearly red-shifted in the case of **NO2PT3**, suggesting that the pull $–NO_2$ group affects the excited state of ~~**NO2PT3**~~ **NO2PT3**, due to the favorite overlapping of π orbitals. ~~At a first glance~~Conversely, the interaction between the *d* orbitals of the silicon atom in the $–Si(OSiMe_3)_3$ group and the π-structure of the terthiophene unit are not able to give an effective interaction. By comparing the **SiPT3** spectrum with that of the ~~molecular model~~ benckmark molecule **SiP**, ~~without any acceptor group and observed in our previous work~~, an almost superimposable (2 nm blue-shifted) band can be observed.[37]

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In addition, a broad absorption band with a very low intensity emerges in the **NO2PT3** spectrum at 705 nm, and can be assigned to an intramolecular charge transfer thus confirming the strong interaction between the aromatic unit and the $–NO_2$ group.

To fully comprehend the effect of silane moiety, a further spectroscopic characterization was conducted by recording the spectra in different solvents. For this purpose, Si- and NO_2-derivatives were dissolved in solvents with increasing polarity by moving from *n*-hexane to MeCN.

A solvatochromic effect is clear for the **NO2PT3** system, while it is just outlined for **SiPT3** (see SM Figure S1 and S2). This suggests that **SiPT3** is not characterized by any strong charge-transfer state in the excited state.

The emission spectra of **SiPT3** and **NO2PT3** are also recorded by revealing very different features. While in the case of **SiPT3** a well-structured emission band at around 472nm can be observed, **NO2PT3** shows weak emission at 506 nm and an intense unstructured band at 700 nm ca. (see Figure 2). The photophysical study helped us to disclose the nature of these bands: at 800 nm a lifetime (τ) of 0.16 ns (χ^2= 1.200) was measured and attributed to an excimer emission, while at 506 nm to the monomer emission with τ= 0.03 ns (χ^2= 1.285, see Figure S3 in the SM). For **SiPT3** only the monomer emission can be observed at 407 nm with τ= 0.29 ns (χ^2= 1.086, see Figure S4 in the SM). The QYs measured in CH_2Cl_2 solution (10^{-5} M) are very low in both **SiPT3** and **NO2PT3**, 0.142 % and 0.023% respectively.

Emission spectrum of **SiPT3** is almost not affected by the polarity of solvent (see Figure S5 in the SM), on the contrary **NO2PT3** is strongly influenced by the nature of solvent, showing a strong solvatochromism and the concomitant excimer formation when the solvent is CH_2Cl_2, $CHCl_3$, acetone or MeCN (see Figure S6 in the SM), thus indicating a stronger charge-transfer state at the ground state.

From the above considerations we can resume that, in contrast with the strong pull $–NO_2$ group, the $–Si(OSiMe_3)_3$ group can be considered innocent from the photophysical point of view, indeed it does not significantly alter the spectroscopic features and because of its steric hindrance, it prevents the formation of excited dimers, *i.e.* excimer species.

Although the monomer emission of **NO2PT3** is only just appreciable, it was possible to measure the spectroscopic HOMO-LUMO gap (2.60 eV) which is slightly narrower than those of **SiPT3** (2.88 eV) and **SiP** (2.91 eV).[37]

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4.3 Electrochemical measurements

The electronic properties of **SiPT3** and **NO2PT3** were also investigated by differential pulse voltammetry (DPV) and compared to the values of **SiP** determined under the same experimental conditions as a benchmark. Complete DPV patterns obtained on a glassy carbon (GC) electrode in 0.1 M tetrabutylammonium perchlorate (TBAP) CH_2Cl_2 solution are reported in Figure 3.

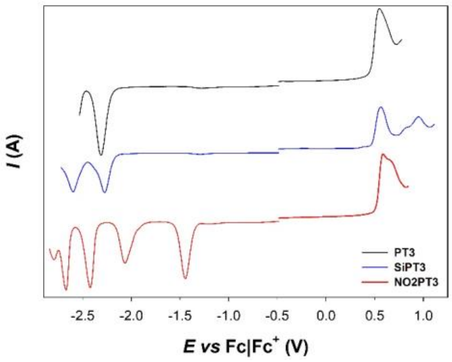

Figure 3. DPV patterns.

In this case DPV analysis allowed a better determination of the peak potentials being more precise than cyclic voltammetry (CV), in fact the oxidation process of a thiophene ring with a free α position is known to promote electrochemical polymerization,[64] which results in a not reversible signal by making difficult the evaluation of the E°'. In all cases at least one oxidation peak and one reduction peaks are observed in the potential window investigated, the first oxidation peak and the first reduction peak of each compounds in principle afford the calculation of formal potentials of first oxidation (anodic) $E^{0'}_{Ia}$ and first reduction (cathodic) $E^{0'}_{Ic}$ processes in the operating solvent (formal potentials $E^{0'}$ approximate standard potentials E^0 under the assumption of neglecting activity coefficients). The experimental $E^{0'}$ values also allow us the evaluation of the electrochemical HOMO and LUMO energy levels and the HOMO–LUMO energy gap E_g (Table 2), employing the ferrocenium/ferrocene redox couple as a reference for intersolvental comparison of electrode potentials.[40,41]

Table 2. Key DPV features of dyes and benchmark, their electrochemical energy levels HOMO and LUMO derived therefrom $E^{0'}_{Ia}$ and $E^{0'}_{Ic}$ (or $E_{p,Ia}$ and $E_{p,Ic}$) all referred to the ferrocene couple.

compound	**$E_{p,Ia}$/V (Fc^+|Fc)**	**$E^{0'}_{Ia}$/V (Fc^+|Fc)**	**$E_{p,Ic}$/V (Fc^+|Fc)**	**$E^{0'}_{Ic}$/V (Fc^+|Fc)**	**HOMO/eV**	**LUMO/eV**	**$\Delta E^{0'}$/V ($E_{g,EC}$/eV)**
PT3	0.54	0.57	-2.31	-2.34	-5.37	-2.46	2.91
SiPT3	0.56	0.59	-2.28	-2.30	-5.39	-2.50	2.89
NO2PT3	0.59	0.61	-1.45	-1.47	-5.41	-3.33	2.08

The first oxidation potential of **SiPT3** is more positive of 0.02 V compared to the one of **SiP**, while **NO2PT3** has the first oxidation peak more positive 0.05 V. This fact indicates that the oxidation of the terthiophene unit is barely affected by the different electron withdrawing group. The presence of the –Si(OSiMe$_3$)$_3$ group moves the first reduction peak to a more positive potential of just 0.04 V, on the contrary for the –NO$_2$ group the reduction peak is more positive of 0.87 V. Therefore, we can conclude that also from the electrochemical point of view the Si-based group is quite innocent on affecting the energy levels of the terthiophene by shifting both the first oxidation and reduction potentials towards more positive potentials, and maintaining almost unchanged the E_g value of 2.~~89~~89 eV when compared to the one of SiP (2.91 eV), ~~which~~ both nicely corresponding to their $E^{0\text{-}0}$ values.
In the case of **NO2PT3**, the –NO$_2$ group does not particularly perturbate the oxidation potential, but the first reduction process occurs at much higher potential, thus a narrower E_g of 2.08 eV is observed. When the –NO$_2$ group is present, the first reduction process is localized on this group,[65] while in **SiP** and in **SiPT3** the oxidation and the reduction process (and therefore also the HOMO and the LUMO) are localized on the same molecular unit and nearly the same values are measured. ~~Thus~~ Therefore, the electrochemical study corroborates the spectroscopic analyses, confirming that ~~the~~ the –Si(OSiMe$_3$)$_3$ group poorly influences the energy levels of the terthiophene unit.

4.4 Second-order NLO measurements

The second order NLO activity of the **SiPT3** chromophore was evaluated by using the EFISH technique and compared directly with that of the analogue **NO2PT3** chromophore. The measurements were carried out under the same experimental conditions (with a non-resonant incident wavelength

@ 1907 nm), in the same solvents (CH_2Cl_2 and DMF) and different concentrations to highlight any effects of aggregation or interaction with the solvents (*e.g.* hydrogen bonds).[66] In addition to the EFISH measurements, the value of the dipole moment of **SiPT3** in chloroform was experimentally measured (see paragraph 2.6) and compared with the theoretical value calculated for **NO2PT3** poorly soluble in this solvent (see paragraphs 2.7 and SM). The data are summarized in the following Table 3.

Table 3. Experimental EFISH and solvatochromic quadratic hyperpolarizabilities measured in different solvents and at different concentrations for **SiPT3** and **NO2PT3**.

Compound	**μ/D**	**Solvent**	**c/M**	**$\mu\beta_{1907}(\times10^{-48})$/esu**	**$\beta_{1907}(\times10^{-30})$/esu**	**$\beta_{CT}(\times10^{-30})$/esu**
SiPT3	3.0	CH_2Cl_2	10^{-3}	290	97	58
		CH_2Cl_2	10^{-4}	480	160	
		DMF	10^{-3}	192	64	
		DMF	10^{-4}	350	116	
NO2PT3	8.3*	CH_2Cl_2	5×10^{-4}	270	33	39
		CH_2Cl_2	10^{-4}	445	54	
		DMF	10^{-3}	260	31	
		DMF	10^{-4}	440	53	

* calculated by DFT calculation with B3LYPfunctional and cc-pTVZbasis. The dipole moments (Debye, D) are computed in the corresponding best molecular geometry. The values have been obtained according to the Polarizable Continuum Model (PCM) mimicking the chloroform solvent.

As expected, **SiPT3** has a dipole moment lower than that of **NO2PT3**, since $–NO_2$ is a better electron acceptor group than the siloxane.

The $\mu\beta_{1907}$ values for both compounds are quite high and positive, suggesting on the basis of the "two-level" model a positive value of $\Delta\mu_{eg}$ and thus an enhancement of the excited state dipole moment in comparison to the ground state one (equation 2). Moreover, they are very similar at the same concentration in the same solvent.

Therefore, not only the SiPT3 "donor-free" system shows unexpected second-order NLO properties, but its quadratic hyperpolarizability β_{1907} is also higher than that of **NO2PT3**, as a result of its lower dipole moment.

The nature of this higher β_{1907} value still remains unclear, as the spectroscopic measurements indicate that there is not a strong conjugation at the ground state between terthiophene and $–Si(OSiMe_3)_3$ acceptor group. It was speculated that a charge redistribution on the population of the excited-state was involved in the charge transfer process favored by the empty *d* orbitals of the silicon or by the σ* orbitals on the Si-based group.[20,38] However, our spectroscopic data do not support this hypothesis, prompting us to look for an explanation elsewhere.

Silicon-based groups are mainly exploited as important tools in organic chemistry, and for this reason the electronic effects of silicon have never been studied in detail from the photophysical point of view. Four electronic effects are known to impact on the ground and excited state of these moieties: inductive effects, field effects, (p-d) π bonding and hyperconjugative effects. The total electronic effect is a combination, at greater or lesser extent, of these effects.[38] Since our electrochemical measurements confirm the spectroscopic data indicating that only the aromatic part of **SiPT3** is mainly involved in the HOMO-LUMO transition, we may, only in a speculative way, suggest that the strong electromagnetic field of the incident laser source produces an unpredictable changing in the electronic properties of the electron system of the -Si(OSiMe$_3$)$_3$ group, with an increment of these effects, in particular the field effect, which is described as the response of π-conjugated system nearly bonded to the dipole moment of the Si-group.[38]

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It is relevant to note that the -Si(OSiMe$_3$)$_3$ moiety does not affect the absorption feature of terthiophene, resulting in an electronic absorption spectrum that is superimposable to that of reference compound **PT3.** Therefore, **SIPT3** shows a net gain in terms of nonlinearity/transparency trade-off, which is a highly desidered requisite for NLO materials.

A deeper analysis of the data in Table 2 indicates that **NO2PT3** is not affected by the nature of the solvent, while on the contrary **SiPT3** shows higher β_{1907} values in less polar and non-coordinating CH_2Cl_2 solvent~~.~~

Moreover, both these ‘donor-free’ NLO-phores show higher $\mu\beta_{1907}$ values at greater dilution by suggesting the formation of aggregates.

By a slow evaporation from a CH_2Cl_2 solution of **SiPT3**, we were able to obtain pale yellow crystals, suitable for X-ray structure determination.

Compound **SiPT3** crystallizes in the P-1 space group with two molecules, labelled with ‘A’ and ‘B’, in the asymmetric unit. Both molecules feature an essentially coplanar terthiophene chain which is partially overlapped with that of the centrosymmetry-related molecule, giving rise to rather slipped head-to-tail J-dimers. In particular, in ‘A dimers’ the thiophene chains are overlapped by only one thiophene ring, with interplanar distance d equal to 3.491 Å, while in ‘B dimers’ (see Figure 4) two thiophene rings are overlapped (d=3.742 Å). Only weak C–H···π interactions connect ‘A’ and ‘B’ molecules in the crystal structure.

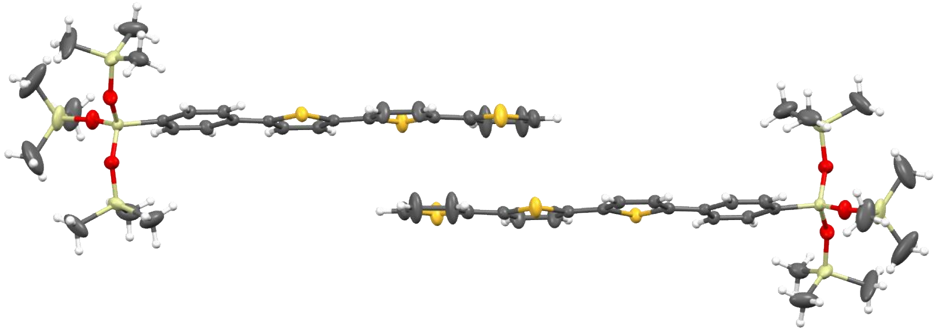

Figure 4. Fragment of **SiPT3** crystal packing showing the dimeric arrangement of ‘B-type’ molecules. Ellipsoids at 50% probability.

Furthermore thiophenic rings are almost coplanar with each other and with respect to the benzene ring and show a herringbone arrangement as predicted by theoretical calculations previously made on these systems.[37]

This kind of J-aggregation is imposed by the cumbersome –Si(OSiMe$_3$)$_3$ group, but in the case of the –NO$_2$ group such a steric hindrance is not present and the formation of alternative head-to-~~tail~~ tail H-aggregates cannot be excluded.

Finally, solvatochromic measurements (see above and SM) provided $\mu\beta_{CT}$ values for both **SiPT3** and **NO2PT3** chromophores (173 × 10^{-48} esu and 315 × 10^{-48} esu, respectively). Nicely the resulting β_{CT}, 58 × 10^{-30} esu and 39 × 10^{-30} esu, are in very good agreement with the β_{EFISH} counterparts, as expected when the direction of the charge-transfer and that of the dipole moment are almost coincident.

In conclusion, from our investigation it seems to emerge that for **SiPT3** there is not a true charge-transfer state in the excited state, *i.e.* the molecule cannot be considered as a classic push-pull system. The reasons for its nonlinear optical activity would therefore not linked to strong conjugation effects at the ground state between the terthiophene and the silicon-based group, as has already been shown by the dipole moment measurements.

Afterwards to gain deeper insights on the origin of the NLO activity of these systems, the analysis was also extended to the other reference chromophores (see Fig. 1), where the acceptor has been eliminated or the donor part has been exchanged with the –NMe$_2$ group.

PT3 has a too low $\mu\beta_{1907}$ value to be assessed: this fact demonstrates that the terthiophene is not NLO-active in the second harmonic generation process without the presence of an acceptor group.

SiPNMe2 and **NO2PNMe2** show second-order NLO properties similar to those of the ‘donor-free’ systems, but display lower $\mu\beta_{1907}$ values.

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Moreover, at 10^{-4} M concentration, **SiPNMe2** shows higher $\mu\beta_{1907}$ values (280×10^{-48} esu in CH_2Cl_2 and 290×10^{-48} esu in DMF) than **NO2PNMe2** (195×10^{-48} esu in CH_2Cl_2 and 230×10^{-48} esu in DMF), confirming the positive effect of the Si-based group. These values also indicate that the terthiophene is a better donor group than the $-NMe_2$ group, even when the latter is the donor group in push-pull chromophores with a more conjugated π-spacer.[20]

Also for **SiPNMe2** and **NO2PNMe2** a solvent effect is observed, having at higher concentration lower μβ values (see Table S2 in SM).

5. Conclusion

In this work, a ‘donor-free’ prototype chromophore, **SiPT3**, consisting of a conducting polymer fragment based on terthiophene, and functionalized with a silicon-based acceptor group was investigated. Although the $-Si(OSiMe_3)_3$ only slightly affects the linear optical properties, *i.e.* absorption and emission properties, and the electronic energy levels of the terthiophene unit, **SiPT3** shows a second-order NLO activity comparable to that observed for the analogous system with ~~a~~ a $-NO_2$ acceptor group, ~~**NO2PT3**~~ **NO2PT3**, characterized by a much higher dipole moment and a strong charge transfer at the excited/ground state. It can be deduced that **SiPT3** is endowed with a higher intrinsic β value; this is also evident when compared ~~to~~ the terthiophene ~~functionalized~~ unit with a typical dimethylamine unit as a donor group.

Finally, it is also noteworthy that, with the same NLO activity, the **SiPT3** chromophore presents a marked improvement in terms of transparency, undergoing a significant blue-shift in its charge-transfer band compared to that of the **NO2PT3** compound. This observation could become particularly useful for the design of new NLO-active chromophores, with a Si-based acceptor unit, as an answer to one of the most typical issue of second-order NLO molecules, namely that of nonlinearity/transparency trade-off for SHG-based devices, and in particular for high-density optical recording, laser printing, and optical measurement systems application~~.~~

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