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High Second-Order NLO Response Exhibited by the First Example of Polymeric Film Incorporating a Diimine-Dithiolate Square-Planar Complex: The [Ni(o-phen)(bdt)]

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Abstract

A novel square-planar diimine-dithiolate non-linear optical (NLO) chromophore, the complex [Ni(o-phen)(bdt)] (1), is reported in this paper (o-phen = dianion of 1,2-phenylenediamina; bdt = 1,2-benzenedithiolate). This compound has been fully characterized by single crystal X-ray diffraction, UV-vis-NIR spectroscopy, cyclic voltammetry, DFT and TD-DFT calculations. 1 crystallizes in the $P_2_1$ space group and shows an almost planar molecule. The cyclic voltammetry measurements present an irreversible anodic peak at 0.87 V and reversible and quasi-reversible reduction waves at $-0.35$ and $-1.13$ V, respectively. A medium-intense ($\varepsilon = 1.91 \cdot 10^4$ mol$^{-1}$dm$^3$cm$^{-1}$) absorption with a maximum at 728 nm appears in the UV-vis-NIR spectrum. The molecular second-order NLO properties of 1 have been measured by Electric Field Induced Second-Harmonic generation technique in DMF solution, giving values of $-1000 \cdot 10^{-48}$ esu for $\mu\beta_{1.0}$ and $-356 \cdot 10^{-48}$ esu for $\mu\beta_0$. Furthermore, remarkable solid-state responses have been measured for polymeric films of 1. Indeed, this complex has been embedded into poly-methyl methacrylate poled films showing high NLO response ($d_{33} = 1.90 \pm 0.38$ pm/V), higher than those previously reported for similar push-pull metal complexes. Moreover, 1 represents the first example of a diimine-dithiolate chromophore incorporated into a NLO-active film.
Introduction

Since the development of lasers several nonlinear optical (NLO) effects, such as second- and third-harmonic generation, stimulated scattering, self-focusing, etc., have been discovered or experimentally proved.\textsuperscript{1-3} Materials showing NLO properties have been extensively investigated in the last decades because of their potential use in telecommunication technologies, optoelectronic and photonic devices.\textsuperscript{1-10}

Molecule-based materials exhibiting second-order NLO properties (\(\beta\) and \(\chi^{(2)}\) at molecular and bulk level, respectively) have received great attention because of their large and fast NLO response and easy processability.\textsuperscript{4-10} So far, different classes of molecular NLO chromophores have been reported in the literature, both “full” organic\textsuperscript{3,11-14} and inorganic. In particular, the latter class comprises push-pull and octupolar complexes of different transition metals showing remarkable \(\beta\) values.\textsuperscript{5-10,15,16} Moreover, different types of reversible switching of the NLO property have been achieved in the case of several complexes.\textsuperscript{17}

For symmetry reasons, only materials without inversion center exhibit second-order NLO effects (\(\beta\) and \(\chi^{(2)}\) \(\neq 0\)).

Among the molecular second-order NLO chromophores, many square-planar push-pull complexes showing remarkable values of \(\beta\) have been reported, in particular dithione-dithiolate\textsuperscript{18-24} and diimine-dithiolate\textsuperscript{5,25-31} compounds. These complexes are formed by a metal ion bound to two ligands with different electron-withdrawing capability. Indeed, the push ligand presents electron-donor groups, which raise the energy level of its orbitals, whereas those of the pull ligand are stabilized by the electron-withdrawing effect due to its substituents. In general, the pull ligand contributes more to the HOMO while the LUMO is predominantly formed by the push ligand (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital).
Because of these features, the solvatochromic HOMO-LUMO transition, which falls in the visible region with a medium molar absorption coefficient and plays a crucial role in the second harmonic generation (SHG, $\beta$ at the molecular level), has a charge transfer (CT) character.\textsuperscript{18-31} By choosing properly the substituents at the periphery of the ligands it is possible to tune the dipole moment of the molecule and the energy of the CT transition, as well as the electronic structure of the frontier orbitals (FOs).

Although the molecules of \textit{push-pull} complexes are noncentrosymmetric ($\beta \neq 0$), very often they crystallize in a centrosymmetric space group preventing the second-order effects occurring at the bulk level ($\chi^{(2)} = 0$). The centrosymmetric arrangement in diimine-dithiolate and dithione-dithiolate complexes, is favored by their intrinsic polarity, due to the different electronic properties of the two ligands. Moreover, even if the crystal packing is non-centrosymmetric, if the molecules show a pseudo-centrosymmetric packing, the $\chi^{(2)}$ value is close to zero.\textsuperscript{32} For these reasons, no dithiolate containing square-planar \textit{push-pull} complexes showing solid state second-order NLO properties have been reported to date. However, because of the paramount importance of NLO response in the solid state for technological applications, in order to overcome this problem, the strategy to incorporate NLO-active molecules in polymeric\textsuperscript{33-37} or hybrid organic-inorganic\textsuperscript{38,39} poled films has been developed and successfully applied to pure organic\textsuperscript{33,34,38,39} and organometallic\textsuperscript{35-37} chromophores.

Surprisingly, despite high first hyperpolarizability values exhibited by the dithiolate square-planar unsymmetrical complexes, NLO studies in bulk of films containing any of these compounds have not been reported in the literature so far, although platinum diamine-dithiolate complexes [Pt(Rbipy)(dmipi)] (dmipi = 4,5-dimercapto-1,3-dithiol-2-propargylimino and $R = H$, t-Bu) have been covalently bound to hydrogen-terminated silicon (100) surfaces.\textsuperscript{40} In this paper we report the
first example of a film incorporating a chromophore of this class of molecules: the novel [Ni(o-phen)(bdt)] (I) complex (o-phen = dianion of 1,2-phenylenediamina; bdt = 1,2-benzenedithiolate). This compound has been embedded into a poly-methyl methacrylate (PMMA) matrix showing remarkably high NLO response. Moreover, I has been fully characterized by single crystal X-ray diffraction, UV-vis-NIR spectroscopy, cyclic voltammetry, DFT and TD-DFT calculations. The second-order NLO response of I were also measured in solution by the Electric Field Induced Second-Harmonic (EFISH) generation technique.

**Experimental Section**

All the reagents and solvents were purchased from Aldrich and used without further purification. The complex [Ni(o-phen)$_2$] was prepared as previously described$^{41}$ whereas [Ni(bdt)$_2$] was synthetized following the same procedure used to prepared the analogue complex$^{42}$ of 3,5-ditertiarybutyl-1,2-benzenedithiolate ligand (yield 80%).

**Preparation**

[Ni(o-phen)(bdt)] (I). *Synthesis*: 210 mg (0.62mmol) of [Ni(bdt)$_2$] in 40 mL of warm DMF, green solution, was added drop-wise to a warm solution of [Ni(o-phen)$_2$] (80 mg, 0.30 mmol) in the same solvent (40 mL). The resulting solution was refluxed 4 hours and then allowed to cool to room temperature (R.T.); after 18 hours of stirring at R.T., the solvent was roto-evaporated and the crude product was partially dissolved with acetone, giving a purple solution. A green-brown solid (49 mg), insoluble in acetone, was separated from the solution by centrifugation. The acetone solution was concentrated until a precipitate appeared and, after the addition of 30 mL of n-hexane, the evaporation of the acetone was completed. A purple microcrystalline solid was collected by centrifugation, washed three times with n-hexane and air-dried (yield 128 mg, 0.42mmol; 70%).
Analytical results are in accordance with the formula [Ni(bdt)(o-phen)]. **Elemental Analysis:**

calculated for C_{12}H_{10}N_{2}S_{2}Ni (305.04): C 47.25, H 3.30, N 9.18; found: C 47.34, H 3.36, N 9.21.

MS (EI): m/z (%) 304.0 (100.00%) [M+]. UV-vis [in DMF; λ, nm (ε, dm^{3}.mol^{-1}.cm^{-1})]: 728 (1.91.10^{4}); 499 (4.04.10^{3}); 355, sh. **FT-IR** (KBr): ν_{max}/cm^{-1} 3260(m); 3090(vw); 3073(vw); 3043(w); 3007(vw); 1600(mw); 1564(w); 1524(w) 1515(mw); 1453(m); 1419(mw); 1382(s); 1367(mw); 1321(w); 1283(mw); 1238(w); 1204(w); 1149(w); 1130(w); 1123(w); 1096(w); 802(vs); 782(mw); 768(m); 726(s); 680(mw); 623(m); 560(w); 450(m).

Elemental Analyses were performed with a Carlo Erba CE1108 Elemental Analyser. MS were carried out on *ThermoElectron MAT 900* by electron impact ionization technique. The UV-vis-near-IR spectra were recorded with a *Jasco V-670* spectrophotometer using a quartz cell of path length 1 cm. IR measurements (4000-400 cm^{-1}) were performed with a spectrophotometer FT-IR Bruker Tensor27 on KBr pellets. Cyclic voltammograms were recorded on an *μAUTOLAB Type III* potentiostat, driven by the GPES electrochemical software; using a conventional three-electrode cell consisting of a platinum wire working electrode, a platinum wire as counter-electrode and Ag/AgCl in saturated LiCl Ethanol solution as reference electrode. The experiments were performed at R.T., in dry and argon-degassed DMF containing 0.1 mol dm^{-3} Bu_{4}NPF_{6} as supporting electrolyte, at 25-200 mV s^{-1} scan rate. Data are quoted against Ag/AgCl; the \( E_{1/2} \) for ferrocene/ferrocinium couple (internal standard) is +0.54 V under the above reported conditions.

Single crystal data were collected at 120 K on an Agilent Technologies SuperNova diffractometer (\( λ = CuK_{α}, 1.54184 \text{ Å} \)). Absorption corrections were done by multi-scan methods using *CrysAlisPro*;\(^{43}\) the structure was solved using Patterson direct charge flipping methods (*Superflip*);\(^{44}\) and refined on \( F^{2} \) with full-matrix squares (*SHELXL*).\(^{45}\) Non hydrogen atoms were refined anisotropically. All H atoms were located in a difference Fourier map and freely refined.
Graphical material was prepared with ORTEP\textsuperscript{46} and Mercury\textsuperscript{47} programs. CCDC 1449051 contains the supplementary crystallographic data for this paper.

\textit{DFT calculations}

Density Functional Theory (DFT)\textsuperscript{48} studies on the ground-state electronic structure of 1 were performed using the GAUSSIAN 09\textsuperscript{49} software package. B3LYP,\textsuperscript{50,51} CAM-B3LYP\textsuperscript{52} (see SI) and PBE1PBE\textsuperscript{53} (SI) were used throughout this investigation as functionals; moreover, the valence triple-zeta 6-311+G(d,p)\textsuperscript{54,55} was employed as basis set for all atoms. More details are given in the SI.

\textit{NLO characterization}

\textit{Solution}. The NLO response of 1 in solution was measured by EFISH experiments\textsuperscript{56,57} as described in ref. 30, using a freshly prepared 10\textsuperscript{-3} M solution of the NLO-phore in DMF (see SI for more details). Solid-state SHG by Kurtz–Perry measurements\textsuperscript{58} were performed as reported in\textsuperscript{59} and summarized in the SI.

\textit{Films}. Details on materials, methods and preparation of the films of 1 in Poly(methyl methacrylate) (PMMA), along with the Corona Poling setup, are reported in SI

\textit{Maker Fringe Measurement}. The absolute second order NLO coefficient matrix values \(d_{ij}\) were obtained by following the standard Maker fringe technique\textsuperscript{60} as described in ref 61.

\textbf{Results and discussion}

Complex 1 has been synthetized in a good yield by refluxing [Ni(bdt)\textsubscript{2}] and [Ni(o-phen)\textsubscript{2}] in DMF as shown in Scheme 1.

Scheme 1. Schematic depiction of the synthesis of 1.
Structural results

Figure 1. (A) Ortep diagram of [Ni(bdt)(o-phen)] (I) with atom labeling and thermal ellipsoids drawn at the 50% probability level; (B) close C—H⋯π and N—H⋯π interactions between adjacent molecules.

Blade-shaped crystals suitable for single crystal X-ray diffraction analysis, were obtained by slow evaporation of a dichloromethane solution. A summary of data collection and structure refinement is reported in Table 1. [Ni(bdt)(o-phen)] crystallizes in the $P_{21}$ space group, which is a non-centrosymmetric group. As discussed in the Introduction, this feature is an essential requirement
for a material to exhibit solid-state second-order NLO properties ($\chi^{(2)} \neq 0$). Unfortunately, in this complex the second-order NLO susceptibility is close to zero (vide infra). A representation of a molecule of $\mathbf{1}$ is reported in Figure 1A; the molecule is almost planar, indeed all non-H atoms are co-planar to within 0.05 Å and the angles between the plane determined by S2NiN2 atoms and those of the benzene rings of the dithiolene and diamine moieties are 5.06° and 2.35°, respectively (Figure S1). The bond distances (see Table 2) are similar to those reported in the literature for other nickel complexes of the same ligands.$^{42,62-64}$ The C—N bond distances are 1.313 and 1.315 Å; these values are smaller than those found for the free ligand (1.406−1.408 Å)$^{65}$ and also than those reported for other diimine-dithiolate

<table>
<thead>
<tr>
<th>Table 1. X-ray crystallographic data for $\mathbf{1}$.</th>
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</thead>
<tbody>
<tr>
<td>Empirical formula</td>
</tr>
<tr>
<td>Formula weight</td>
</tr>
<tr>
<td>Colour, habit</td>
</tr>
<tr>
<td>Crystal size, mm</td>
</tr>
<tr>
<td>Crystal system</td>
</tr>
<tr>
<td>Space group</td>
</tr>
<tr>
<td>a, Å</td>
</tr>
<tr>
<td>b, Å</td>
</tr>
<tr>
<td>c, Å</td>
</tr>
<tr>
<td>β, deg.</td>
</tr>
<tr>
<td>V, Å$^3$</td>
</tr>
<tr>
<td>Z</td>
</tr>
<tr>
<td>T, K</td>
</tr>
<tr>
<td>$\rho$ (calc), Mg/m$^3$</td>
</tr>
<tr>
<td>$\mu$, mm$^{-1}$</td>
</tr>
<tr>
<td>$\theta$ range, deg.</td>
</tr>
<tr>
<td>No. of rflcn/unique</td>
</tr>
<tr>
<td>Goof</td>
</tr>
<tr>
<td>R1$^a$</td>
</tr>
<tr>
<td>wR2$^b$</td>
</tr>
</tbody>
</table>

$^a$R1 = $\Sigma||F_o|-|F_c||/\Sigma|F_o|; $^b$wR2 = $[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, where P = $[\max(F_o^2,0) + 2F_c^2]/3$
complexes (1.350−1.368 Å). These data strongly support a behavior as diimine of the o-phen ligand in complex ı.

**Electrochemical studies**

The DMF cyclicvoltammogram of ı (Figure 2) presents an irreversible anodic peak at 0.87 V (0 → +1) and reversible ($i_c/i_a \cong 1$) and quasi-reversible reduction waves at −0.35 (0 ζ −1) and −1.13 V (−1 ζ −2), respectively. These values show that the electrochemical properties of ı are in between those of the corresponding homoleptic complexes. Indeed, in the case of [Ni(o-phen)$_2$], the oxidation and the first reduction processes are both reversible and fall at 0.18 and −0.83 V, whereas for [Ni(bdt)$_2$]$^-$ the peaks corresponding to the same processes fall at 1.40 and 0.17 V, respectively.

**Table 2.** Comparison of experimental and B3LYP calculated bond lengths (Å) and angles (°) for ı.

<table>
<thead>
<tr>
<th>Bond Combination</th>
<th>Experimental</th>
<th>B3LYP Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(1)-S(1)</td>
<td>2.1226(5)/2.152</td>
<td>S(1)-Ni(1)-S(2)</td>
</tr>
<tr>
<td>Ni(1)-S(2)</td>
<td>2.1175(5)/2.152</td>
<td>S(1)-Ni(1)-N(2)</td>
</tr>
<tr>
<td>Ni(1)-N(1)</td>
<td>1.863(2)/1.878</td>
<td>S(1)-Ni(1)-N(1)</td>
</tr>
<tr>
<td>Ni(1)-N(2)</td>
<td>1.873(2)/1.878</td>
<td>S(2)-Ni(1)-N(1)</td>
</tr>
<tr>
<td>C(1)-S(1)</td>
<td>1.747(2)/1.748</td>
<td>N(1)-Ni(1)-N(2)</td>
</tr>
<tr>
<td>C(2)-S(2)</td>
<td>1.744(2)/1.748</td>
<td>Ni(1)-S(1)-C(1)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.405(3)/1.413</td>
<td>Ni(1)-N(1)-C(7)</td>
</tr>
<tr>
<td>N(1)-C(7)</td>
<td>1.313(2)/1.325</td>
<td>S(1)-C(1)-C(2)</td>
</tr>
<tr>
<td>N(2)-C(8)</td>
<td>1.315(2)/1.325</td>
<td>N(1)-C(7)-C(8)</td>
</tr>
<tr>
<td>C(7)-C(8)</td>
<td>1.465(3)/1.458</td>
<td></td>
</tr>
</tbody>
</table>
Figure 2. Cyclic voltammograms of \(1\) recorded at different scan rates in a DMF solution.

**UV-vis-NIR measurements**

The UV-vis-NIR spectrum of \(1\) is shown in Figure 3a. It presents a shoulder at 355 nm and a medium and a medium-intense absorption (dm\(^3\)·mol\(^{-1}\)·cm\(^{-1}\)) at 499 (4.04·10\(^3\)) and 728 nm (1.91·10\(^4\)), respectively. The latter band, which is the most important in NLO property generation, corresponds to a HOMO-LUMO transition and shows a moderate negative (hypsochromic shift) solvatochromic effect (Figure 3b), confirming the CT character of this transition in agreement with the computational results (vide infra). In \(1\) the solvatochromic effect is remarkably smaller (26 nm) than those found for other diimine-dithiolate\(^{30,31,69}\) and dithione-dithiolate\(^{20,21}\) complexes (80-140 nm). Furthermore, the energies of the maxima of the solvatochromic bands present a linear behaviour vs solvent polarity parameters \((r^2 > 0.939)\) as proposed by Eisenberg for several Pt-diimine-dithiolate compounds\(^{69}\) (Figure S6a); as expected, the solvatochromic shift, obtained from the plot’s slope, is smaller (0.074) than those reported in ref. 69 and for other push-pull compounds\(^{20,21,30,31}\) in agreement with the smaller solvatochromic effect exhibited by \(1\). Similar trend \((r^2 > 0.938)\) is also observed when Reichardt’s solvent polarity parameters are used (Figure S6b).\(^{70}\)
Figure 3. (A) UV-vis-NIR spectrum of 1 in DMF; (B) Solvatochromic effect of complex 1 in DMF/CS$_2$ mixtures with different ratios.

Computational studies

The electronic structure of 1 has been investigated by DFT calculations at B3LYP/6-311+G(d,p) level of theory. The optimized geometry in the gas-phase is depicted in Figure S7. The calculated structure is planar, and both bond distances and angles are in very good agreement with the crystallographic data (see Table S2). The molecular orbitals of 1 calculated in the gas-phase are shown in Figure 4. The frontier orbitals (FOs) and the HOMO−1 present a π-symmetry, while the LUMO+1 is a σ-type orbital. The calculated fragment contributions to the FOs (see Table 3) show an electronic delocalization extended over the two ligands. Indeed, the
contributions to the HOMO from the o-phen (*push*) and from the bdt (*pull*) are 30.1 and 67.1%, respectively. In the LUMO orbital these contributions are 29.5% from the dithiolate and 58.5% from the diimine; moreover, also the metal’s contribution to this MO is important (12.0%). Although each FOs has remarkable contributions from all the different fragments, the HOMO-LUMO transition has a significant CT character, more precisely, a ligand-to-mixed-metal-ligand CT character. The contributions calculated for 1 are significantly different from those found for other diimine-dithiolate complexes\(^{30,31,66}\) (84.2−77.2% to the HOMO and 91.4−79.8% to the LUMO from the dithiolate and diimine ligand, respectively). The more extended delocalization presented by 1, seems to stabilize both the FOs in comparison with those of the above cited diimine-dithiolate compounds (−5.54 vs −4.50/−4.96 eV and −3.85 vs −2.93/−3.39 eV for HOMO and LUMO, respectively). These complexes show a solvatochromic effect stronger than 1, according to a more pronounced CT character presented by their HOMO-LUMO transitions.\(^{30,31,66}\) The smaller dipole moment (\(\mu\)) calculated for 1 (4.42 D) is also in agreement with the differences in the electronic structures observed between this compound and other diimine-dithiolate complexes (\(\mu = 8.07−11.15\) D).\(^{30,31}\)
Table 3. Comparison of calculated fragment contributions and energy levels of the FOs in gas-phase and DMF of complexes 1.

<table>
<thead>
<tr>
<th>Phase</th>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Energy (eV)</td>
<td>bdt (%)</td>
</tr>
<tr>
<td>Gas</td>
<td>−5.544</td>
<td>67.1</td>
</tr>
<tr>
<td>DMF</td>
<td>−5.737</td>
<td>77.9</td>
</tr>
</tbody>
</table>

With the aim to evaluate the effect of the solvation on the electronic structure of 1, DFT calculations in DMF, modelled by the CPCM, have been done. These studies show that, in comparison with the gas-phase, the solvation induces a greater polarization in the molecule, as evinced from the composition of the frontier orbitals (Table 3) and the calculated $\mu$ (10.22 D). Moreover, the solvation also affects the energy of the orbitals (Table 3) although not in the same manner; indeed it stabilizes the HOMO more than the LUMO increasing the energy gap. The charge redistribution associated to the solvent-induced polarization, is evident by comparison of the electrostatic potentials, mapped on electron density isosurfaces, calculated for 1 in the gas phase and DMF (Figure S8). Indeed, the solvation affects the charge separation between the two ligands, increasing the negative charge over the dithiolate one. Time dependent DFT calculations have been performed in order to investigate the electronic transitions of 1 in both, gas phase and DMF. The calculated electronic spectrum in DMF is in very good agreement with the experimental one, measured in the same solvent (Figure S9). The transition at 728 nm presents a molar extinction coefficient ($1.91 \times 10^4 \text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) remarkably higher than those found for other compounds of the same class ($2.50-6.00 \times 10^3 \text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). $^{30,31,66}$ This finding is strongly in agreement with the calculated values of the oscillator strength ($f$) which is related to the intensity of the electronic
transition. Indeed, f calculated in DMF is 0.433 for 1 whereas it ranges between 0.130 and 0.155 for the other complexes.\textsuperscript{30,31}

**NLO properties**

The 2\textsuperscript{nd} order NLO properties of 1 have been investigated by the EFISH method,\textsuperscript{56} with measurements performed in DMF using an incident laser beam at 1.907 \(\mu\)m of wavelength. EFISH experiments give a measure of the scalar product \(\mu\beta_i\), where \(\mu\) is the molecular dipole moment and \(\beta_i\) the vector part of the quadratic hyperpolarizability tensor; \(\beta_i\) depends from the frequency of the incident light. The static quadratic hyperpolarizability \(\beta_0\), is the extrapolated value to zero frequency and can be calculated taking into account the wavelength of the maximum of the absorption of the CT transition of the chromophore. The NLO response of 1 was \(-1000 \cdot 10^{-48}\) esu for \(\mu\beta_i\) which corresponds to a value of \(-356 \cdot 10^{-48}\) esu for \(\mu\beta_0\). The negative value is in agreement with the observed negative solvatochromism. More notably, despite the small solvatochromic effect exhibited by 1 in comparison with those of the above cited diimine-dithiolate complexes,\textsuperscript{30,31} the NLO response of 1 is quite high. For example, it appears higher than those reported for the first examples of Ni(II) diimine-dithiolate complexes\textsuperscript{28} and comparable to that reported by some of us for [Ni(4,4'-dimethylcarboxy-bpy)(bdt)], carrying an electron-withdrawing group.\textsuperscript{30} An explanation of this finding can be obtained taking into account a simplified model, the two-state one\textsuperscript{71-74} (equation 1) which provides a relationship between \(\beta_0\) (the static quadratic hyperpolarizability), \(\lambda_{\text{max}}\) (the maximum of the HOMO-LUMO transition), \(f\) and the difference between the ground and excited-state dipole moments (\(\Delta\mu_{\text{ge}}\)).

\[
\beta_0 = 1.617 \lambda_{\text{max}}^3 f \cdot \Delta\mu_{\text{ge}}
\]

(1)

The two-state model, even though is a simplification, furnishes a qualitatively good correlation between the characteristic of the molecules and their second-order NLO properties, as
demonstrated for other push-pull chromophores both, organic\textsuperscript{11} and inorganic.\textsuperscript{18-21,30,66,75,76} In the case of complex 1, the high value of the oscillator strength (see above) seems to play a crucial role in determining the NLO response of this complex, partially compensating the small difference of the dipole moment between the ground and excited-state ($\Delta \mu_{ge}$ is related to the solvatochromic effect).

Because 1 crystallizes in a non-centrosymmetric space group, its second-order NLO properties have been investigated also at the solid state by Kurtz–Perry measurements\textsuperscript{58}. Unfortunately, despite its symmetry, 1 is incapable of SHG in the crystal form; this is probably due to the molecular packing with a pseudo-centrosymmetric arrangement, which induces an almost null value for $\chi^{(2)}$.\textsuperscript{32}

\textit{NLO properties of the PMMA films}

The 2\textsuperscript{nd}-order NLO response of 1 in the solid state was achieved incorporating the chromophore into a poled PMMA film. Through the corona wire poling process at high temperature a non-centrosymmetric alignment of 1 in the PMMA film was reached, monitoring the SHG signal in situ during the poling and at RT after the electric field was switched off. The PMMA film was obtained by spin-coating. After the deposition of the film onto the glass substrate, the latter was rinsed with acetone on the side not containing the film, so to remove any residue left by the deposition phase. Before poling, the film was stored in the dark in air. Before and after poling, the electronic absorption spectrum of the 1/PMMA film was recorded (Figure S10). The shape of the main absorption band is very similar to that obtained in DMF solution (Figure 3), thus confirming that in the film there are no aggregates and that the PMMA matrix has no influence on the electronic structure of the NLO-phore. Comparing the spectra before and after poling, no perceivable Stark shift of the main absorption band is observed, while the decrease of the intensity
of the band after poling can be due to dichroism effect,\textsuperscript{77,78} caused by the reorientation of the NLO-phore molecules in the polymeric matrix, given that no significant sublimation is detected during the poling experiments.

As already reported in the literature,\textsuperscript{79-81} a linear relationship between the $d_{33}$ coefficient (the figure of merit of the electro-optical properties) and the loading of a NLO chromophore in a PMMA film exists. However, in the present investigation a low loading (4\%) was chosen to prevent aggregations of the NLO-phores. As a consequence, the $d_{33}$ value of the composite PMMA films investigated were very low.

For the poling experiments a Q-switched Nd:YAG laser (producing a 1064 nm incident wavelength) was used and the SHG signal was recorded in situ. The standard Maker fringe technique afforded a quantitative evaluation of the $d_{33}$ coefficient. The thickness of the poled films was measured by profilometry. Before poling, three vacuum-nitrogen cycles were applied to the film, placed inside a specially built dry-box, so to lower the oxygen level as much as possible. In the poling process the ozone produced by the high electric field could quickly lead to a rapid and irreversible degradation of the film. For this reason performing the measure under nitrogen atmosphere is mandatory. The corona wire poling dynamic of the SHG of the investigated PMMA films are depicted in Figure 5. The SHG was negligible at room temperature. After application of the electric field, at the beginning the signal remained very low, but after 25 min it abruptly increased reaching its maximum value after 40 min. After the plateau was reached, the temperature was decreased to 20°C, and the loss of the SHG signal was only 20\%.
Figure 5. *In situ* corona wire poling dynamic of the SHG of the PMMA film containing the complex 1.

However, the most notable observation is that after removal of the applied electric field the SHG signal remained almost constant, showing a decrease only when the sample was moved from nitrogen to air atmosphere. At this stage, the decreasing of the SHG signal is expected due to the decrease of the local surface electric field.82 The second order NLO coefficient matrix value \(d_{33}\) for poled films was obtained by following the standard Maker fringe technique60 (Figures S11-S13), obtaining a remarkable value of 1.90 ± 0.38 pm/V, higher than those previously reported for similar push-pull metal complexes.36,37 Moreover, it is noteworthy that these compounds show NLO responses at the molecular level (\(\beta\)) higher than that exhibited by 1.36,37

Conclusions

We prepared and characterized 1, a novel push-pull diimine-dithiolate NLO chromophore. The X-ray data show a square-planar molecular structure and bond distances in agreement with a depiction of this compound as a diimine-dithiolate complex. Spectroscopic and computational studies have shown that the optical absorption at 728 nm arises from a HOMO-LUMO transition. Although with different contributions from the two ligands, both of the frontier orbitals are delocalized over the all molecule reducing the CT character of this transition, in agreement with
the observed small solvatochromic effect. Despite these findings, 1 presents a good NLO response which can be explained taking into account the two-state model (equation 1) and the high value of \( f \) related to the HOMO-LUMO electronic transition. The molecular second-order NLO properties of 1 were measured by EFISH method, giving values of \(-1000\) and \(-356\cdot10^{-48}\) esu for \( \mu\beta_{1.907} \) and \( \mu\beta_0 \), respectively. This complex has been also incorporated into PMMA poled films exhibiting remarkably high NLO response \( (d_{33} = 1.90 \pm 0.38\, \text{pm/V}) \), higher than those showed by similar push-pull metal complexes. Notably, 1 represents the first example of diimine-dithiolate chromophore incorporated into a NLO-active film. Encouraged by these results, we will prepare films incorporating diimine-dithiolate complexes showing values of \( \beta \) significantly higher than 1,\(^{25-31}\) with the aim to achieve better solid-state NLO responses and to elucidate the structure-properties relationship.

ASSOCIATED CONTENT

Supporting Information.

Electronic Supplementary Information (ESI) available: pictures of crystal structure of 1 (Figures S1-S5); list of Van der Waals contacts (Table S1); solvatochromic peak vs solvent polarity parameters (Figure S6) DFT-optimized geometry (Figure S7); comparison between experimental and calculated structural data (Table S2); electrostatic potential mapped on electron density isosurfaces (Figure S8); calculations with CAM-B3LYP and PBE1PBE as functionals; DMF calculated and experimental electronic spectra (Figure S9); frontier orbitals (Tables S3 and S4); HOMO and LUMO energies and compositions orbitals (Tables S5 and S6); electronic absorption spectra in the PMMA film (Figure 10); Maker fringe (Figures S11-S13); Hirshfeld surface (HS)
analysis (Figures S14-S17). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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