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Second-Order NLO Switches from Molecules to Polymer Films Based on Photochromic Cyclometalated Platinum(II) Complexes

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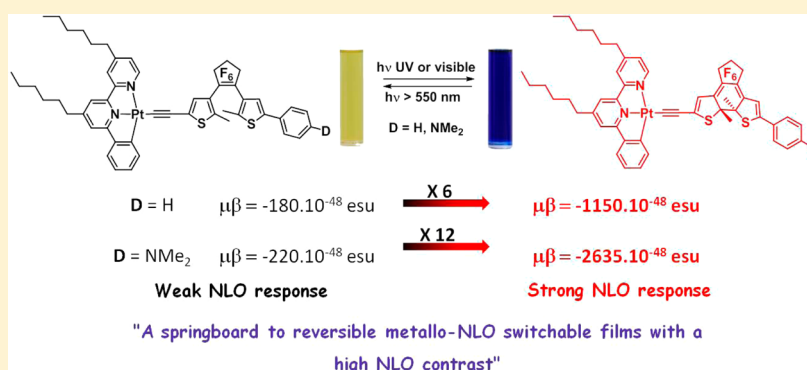
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S Supporting Information



ABSTRACT: Novel photochromic dithienylethene-based platinum(II) complexes $(C^{\wedge}N^{\wedge}N)Pt(C\equiv C-DTE-C_6H_4-D)$ ($(C^{\wedge}N^{\wedge}N) = 4,4'$ -di(*n*-hexyl)-6-phenyl-2,2'-bipyridine; D = H, NMe₂) were prepared and characterized. Their excellent photochromic properties allow the photoinduced switching of their second-order nonlinear optical properties in solution, as measured by the EFISH technique, due to formation of an extended π -conjugated ligand upon suitable electromagnetic radiation. Insights into the electronic structures of the complexes and the nature of their excited states have been obtained by DFT and TD-DFT calculations. These novel Pt(II) complexes were nanoorganized in polymer films which were poled, affording new materials characterized by a good second-order NLO response that can be easily switched, with an excellent NLO contrast. To the best of our knowledge, our compounds allowed designing the very first examples of switchable NLO polymer films based on metal complexes.

INTRODUCTION

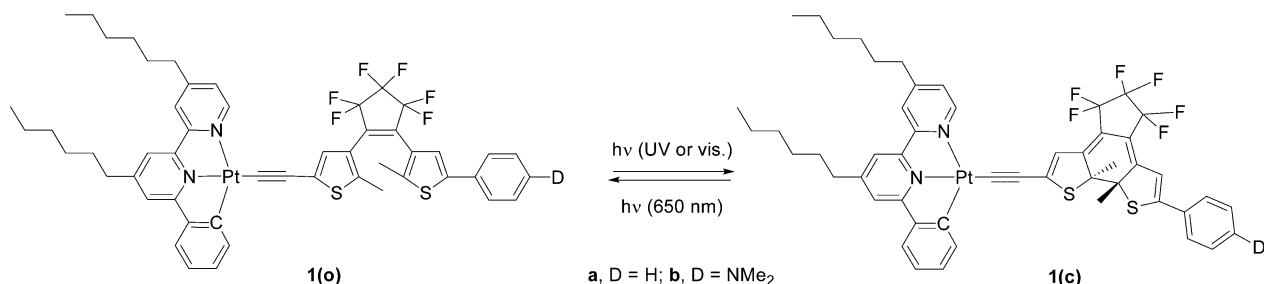
During the last two decades, compounds with large second-order nonlinear optical (NLO) properties have been extensively investigated in view of their large panel of applications, for example, as molecular building blocks for optical communications, optical data processing and storage, or electrooptical devices.¹ Among them molecular species with commutable NLO properties are of growing interest because incorporation of switchability into the NLO behavior of such molecular materials increases their potential for novel applications in emerging optoelectronic and photonic technologies.² Thus, modulating the electronic and optical

properties using an external trigger has been extended to the field of nonlinear optics, and in recent years, there have been numerous works devoted to the switching of the second-order NLO response at the molecular level. The quadratic hyperpolarizability of chromophores may be manipulated by reversibly modifying the properties of specific parts of active molecules. The on/off switching may involve reducing the donor capacity of the electron-rich fragment of a typical donor(D)–acceptor(A) species, D-linker-A, by oxidation or

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Scheme 1. Photocyclization of Complexes 1a,b



protonation.² Conversely, the acceptor behavior of A can be altered by reduction or deprotonation. Alteration of the quadratic hyperpolarizability may also involve structural or chemical modification of the bridging group, thereby interfering with the communication between D and A. Thus, second-order NLO switches can be achieved by a pH variation, by a redox process, or by interaction with an electromagnetic radiation.²

Remarkably, coordination complexes may offer additional flexibility when compared to organic NLO chromophores by introducing NLO active charge-transfer transitions between the metal and the ligands, tunable by virtue of the nature, oxidation state, and coordination sphere of the metal center and even by the number of f electrons.³ Considerable effort has been made in designing and preparing coordination complexes with effective redox- or photoswitchable second-order NLO response in solution.^{2,4} Because metal complexes showing both luminescent and second-order NLO properties are particularly appealing as molecular multifunctional molecular materials,⁵ we have been exploring in the past decade the design and synthesis as well as the linear and nonlinear properties of several metal complexes as NLO and luminophores. In particular, we developed reversible metallo-NLO switches using coordination chemistry as a strategy allowing elaboration of multiphotochromic metal complexes, presenting an efficient phototriggered quadratic NLO enhancement in the liquid phase. For this purpose, we used the ubiquitous photochromic dithienylethene (DTE) unit⁶ and demonstrated the photomodulation of the NLO responses in solution of several DTE-based bipyridine metal complexes⁷ (Zn, Cu, and Fe). In addition, luminescence properties can be photomodulated using the same photochromic bipyridine ligand coordinated to a bis-cyclometalated Ir(III) moiety.⁸ Strikingly, we found that in the case of (bipyridyl)Re and Ru complexes both kinds of optical properties can be photo-regulated within the same complex.

It is known that cyclometalated platinum complexes display rich photophysical properties,¹⁰ and preparation of related photochromic complexes for photoregulation of their luminescence properties has been intensively developed.¹¹ However, the NLO activity of cyclometalated Pt(II) complexes remains less explored. Investigations on cyclometalated phenylpyridine complexes of the type (C^N^N)Pt(II), featuring a β -(diketonate) coligand, and cyclometalated dipyritylbenzene complexes of the type (N^C^N)Pt(II), fascinating for their excellent brightness and luminescent properties,¹² produce large NLO responses.^{13,14} Interestingly, the charge transfer in these systems that controls both the linear and the nonlinear optical properties can be readily modulated by chemical modification of the ligands. The ability to switch *on* and *off* the second-order NLO response of cyclometalated Pt(II) complexes is particularly appealing, and a density functional theory

investigation showed that it can be achieved using well-designed photochromic DTE ligands.¹⁵

On the other hand, since the electronic mechanisms which yield the NLO response in molecular systems are well defined, it is now crucial to face their molecular engineering in order to obtain organized molecular materials showing a temporal stable and high bulk second-order NLO response.¹⁶ While at the molecular level there is an increasing number of scientific contributions about the NLO switching of coordination compounds,² at the macroscopic level this aspect has been scarcely demonstrated.¹⁷ Actually, very few examples of organized molecular materials with a high and switchable NLO response are reported to date, such as the redox switching of the NLO response of Langmuir–Blodgett films based on Ru(II) complexes.^{17c,d}

Surprisingly, although a large panel of redox-active² and photochromic metal complexes¹⁸ has appeared, there are, to the very best of our knowledge, *no examples of reversible metallo-NLO switch in the solid state so far*. Nevertheless, DTE derivatives exhibit good photochromic properties in the solid state, in thin films, or in the crystalline state,¹⁹ and their linear optical properties have been successfully switched in polymer films. For instance, high contrast fluorescence switching and erasable optical recording was demonstrated in high-loaded solid media.²⁰ Photoswitching of the second-harmonic generation (SHG) from poled phenyl-substituted DTE thin films in a polystyrene matrix and their second-order NLO properties in solution, measured by the electric-field-induced second-harmonic generation (EFISH) technique,²¹ have been recently reported by some of us.²²

With our expertise in the luminescence studies of cyclometalated platinum(II) alkynyls,²³ we reasoned that this class of compounds may be appealing candidates for metallo-NLO switches in both solution and polymer films, as they provide access to multifunctional materials. Moreover, mono-DTE-based systems appear more appropriate for this first study than the multiphotochromic bipyridyl metal complexes previously reported by our groups. We describe herein the synthesis of the new photochromic DTE-based platinum(II) complexes (C^N^N)Pt(C≡C-DTE-C₆H₄-D) **1a,b** ((C^N^N) = 4,4'-(*n*-hexyl)-6-phenyl-2,2'-bipyridine; **a**, D = H; **b**, D = NMe₂; Scheme 1). Their excellent photochromic properties allow photoinduced switching of their second-order NLO properties. A significant enhancement of the NLO response $\mu\beta$ measured by the EFISH technique is observed as a result of the formation of an extended π -conjugated ligand. Addition of the electron-donating amino substituent on the alkyne ligand in **1b** leads to an increase of the quadratic hyperpolarizability of the closed DTE form. Insights into the electronic ground- and excited-states structures of the complexes have been obtained by DFT and TD-DFT calculations.²⁴

EXPERIMENTAL SECTION

Synthesis. Compounds **L'a**^{11a} and $[(C^{\wedge}N^{\wedge}N)PtCl]^{10a}$ ($(C^{\wedge}N^{\wedge}N)$: 6-phenyl-4,4'-bis(*n*-hexyl)-2,2'-bipyridine) were prepared following reported procedures. The new compound **L'b** was prepared similarly to **L'a**, whereas the novel DTE-based platinum(II) complexes $(C^{\wedge}N^{\wedge}N)Pt(C\equiv C-DTE-C_6H_4-D)$ **1a,b** were prepared by coupling the appropriate chloro precursor $(C^{\wedge}N^{\wedge}N)PtCl$ with the DTE-based alkyne **L'** (see Supporting Information for details of the syntheses and characterization of the various compounds, Scheme S1).

Polymer Films: Preparation and Characterization. Composite films were produced by casting assisted by a control coater on glass substrates from a dichloromethane solution of a poly(methyl methacrylate) (PMMA, $M_w \approx 15000$; $T_g = 86.5$ °C as determined by differential scanning calorimetry) matrix (75 mg/mL) and complex **1a** or **1b** in closed form (6% w/w relative to the polymer). The spinning parameters were set at the following values: RPM 1 = 700; ramp 1 = 1 s, time 1 = 5 s; RPM 2 = 2000; ramp 2 = 5 s, time 2 = 80 s. Complexes **1a(c)** and **1b(c)** (c = closed form) film thickness was measured by ellipsometry to be 1.49 and 1.7 μm , respectively. UV-vis absorption spectra of photochromic films were carried out using a JASCO V570 spectrometer. Concentrations of the photochromic complexes in the films were calculated from their optical spectra to be 0.15×10^{20} (complex **1a(c)** film) and $0.22 \times 10^{20} cm^{-3}$ (complex **1b(c)** film).

Corona Poling Setup. The fundamental incident light was generated by a 1064 nm Q-switched Nd:YAG (Quanta System Giant G790–20) laser with a pulse of 7 ns and 20 Hz repetition rate. The output pulse was attenuated to 0.57 mJ and focused with a lens ($f = 600$ mm) on the sample, placed over the hot stage. Corona poling process was performed inside a drybox in a N_2 atmosphere. The fundamental beam was polarized in the incidence plane (so-called p polarized) with an angle of about 55° with respect to the sample in order to optimize the SHG signal. The hot-stage temperature was controlled by a GEFRAN 800 controller, while the corona-wire voltage (up to 8.5 kV across a 10 mm gap) was applied by a TREK 610E high-voltage supply. After rejection of the fundamental beam by an interference filter and a glass cutoff filter, the p-polarized SHG signal at 532 nm was detected with a UV-vis photomultiplier (PT, Hamamatsu C3830). The output signal from the PT was set to a digital store oscilloscope and then processed by a computer with dedicated software.

Maker Fringe and Second-Harmonic Photoswitch. In the Maker fringe experiment, the second-harmonic (SH) intensity was detected as a function of the incidence angle of the fundamental beam and normalized with respect to that of a calibrated quartz crystal wafer (X-cut) 1 mm thick whose d_{11} is 0.46 pm/V. The incidence angle was changed by rotating the poled film along the Y axis (Figure 1), while

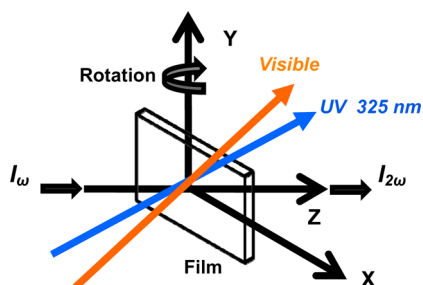


Figure 1. Set-up photoswitch experiment and maker fringe (XYZ is the macroscopic coordinate system).

the polarization of the fundamental and SH beam could be changed by a half-wave plate and a cube beam splitter, respectively, as previously reported.²⁵ In order to determine the nonzero independent components of the susceptibility tensor for poled films ($C_{\infty v}$ symmetry) Maker fringe measurements were conducted with different polarizations: $p \rightarrow p$, $s \rightarrow p$, and $45 \rightarrow s$. In the SHG photoswitch experiment the poled film was rotated at an incidence angle of 57° and

the fundamental and SH beams were p polarized. The poled film was alternately irradiated by a He–Cd laser (Kimmon IK53S2R-D) at 325 nm (continuous wave (cw) mode power, 15 mW) and visible light with a cutoff filter at 550 nm (cw mode power, 157 mW) in order to change the state of the photochromic molecules. The two beams crossed the poled film in noncollinear configuration with respect to the fundamental beam, and beam widths were about 1 cm.

RESULTS AND DISCUSSION

Synthesis of the Complexes. The DTE-based platinum(II) complexes $(C^{\wedge}N^{\wedge}N)Pt(C\equiv C-DTE-C_6H_4-D)$ **1a,b** were prepared by coupling the appropriate chloro precursor $(C^{\wedge}N^{\wedge}N)PtCl^{10a}$ with the DTE-based alkyne **L'** (see Supporting Information for details of the syntheses and characterization of the various compounds, Scheme S1). Compound **L'b** was synthesized following the procedure reported for **L'a**.^{11a} Complexes **1** were isolated as orange powders in good yields and characterized by 1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. The 1H NMR spectrum ($CDCl_3$) of **1a** (see Figure S1, Supporting Information) in its open form (o) shows two characteristic singlets for the nonequivalent methyl protons ($\delta = 2.01, 1.87$ ppm).

Photophysical Properties and Photocyclization Reactions. Measured absorption spectra of complexes **1a,b** in their open forms are presented in Figure 2A, whereas the characteristic data are collected in Table 1. The spectrum of **1a(o)** displays an intense band (365 nm in CH_2Cl_2) in the UV region corresponding to a mixed character of $IL(\pi \rightarrow \pi^*)$ transitions of the $C^{\wedge}N^{\wedge}N$ and the DTE-acetylide ligands, consistent with the calculations (see below). In the visible region, a broad band is observed at 450 nm, tailing up to 540 nm, corresponding to the metal-to-ligand charge transfer [$MLCT d\pi(Pt) \rightarrow \pi^*(C^{\wedge}N^{\wedge}N)$] with some mixing of ligand to ligand charge transfer transition [$L'LCT (\pi(C\equiv C-DTE-Ar) \rightarrow \pi^*(C^{\wedge}N^{\wedge}N))$]. For **1b(o)**, an additional intense band is observed at 325 nm which is ascribed to the $IL(\pi \rightarrow \pi^*)$ transitions of the (dimethylamino)aryl-substituted thiophene fragment as a result of the presence of a pushing end group. The low-energy $MLCT/L'LCT$ band remains unaffected by the presence of the dialkylamino group, consistent with a poorly conjugated open form.

The photocyclization reactions have been monitored by UV-vis absorption and 1H NMR spectroscopies. Figure 2B depicts the electronic spectra of the closed isomers at the photostationary state (PSS) upon irradiation at 350 nm of a CH_2Cl_2 solution of **1a** and **1b**, and the corresponding numerical data are listed in Table 1. The emergence of a new low-energy band in the visible domain is typical of formation of closed DTE.¹¹ The transition band attributed to the closed-DTE unit of **1a(c)** appears at 616 nm, while introducing an amino group in **1b** induces both a small red shift (633 nm) and a broadening of this hallmark band. Moreover, in both cases, the 1H NMR experiments show quantitative formation (95% conversion) of the closed form **1a,b(c)** (Figure S1, Supporting Information). Excitation into the visible ($MLCT$ band) leads to the same photochromic behavior: a similar rate of conversion to **1a,b(c)** is observed. This feature, already reported in related systems, suggests a possible cyclization pathway via the 3MLCT excited state.¹¹

DFT and TD-DFT study. Starting from the optimized geometries obtained at the PBE0/LanL2DZP level (computational details in the Supporting Information) vertical TD-DFT

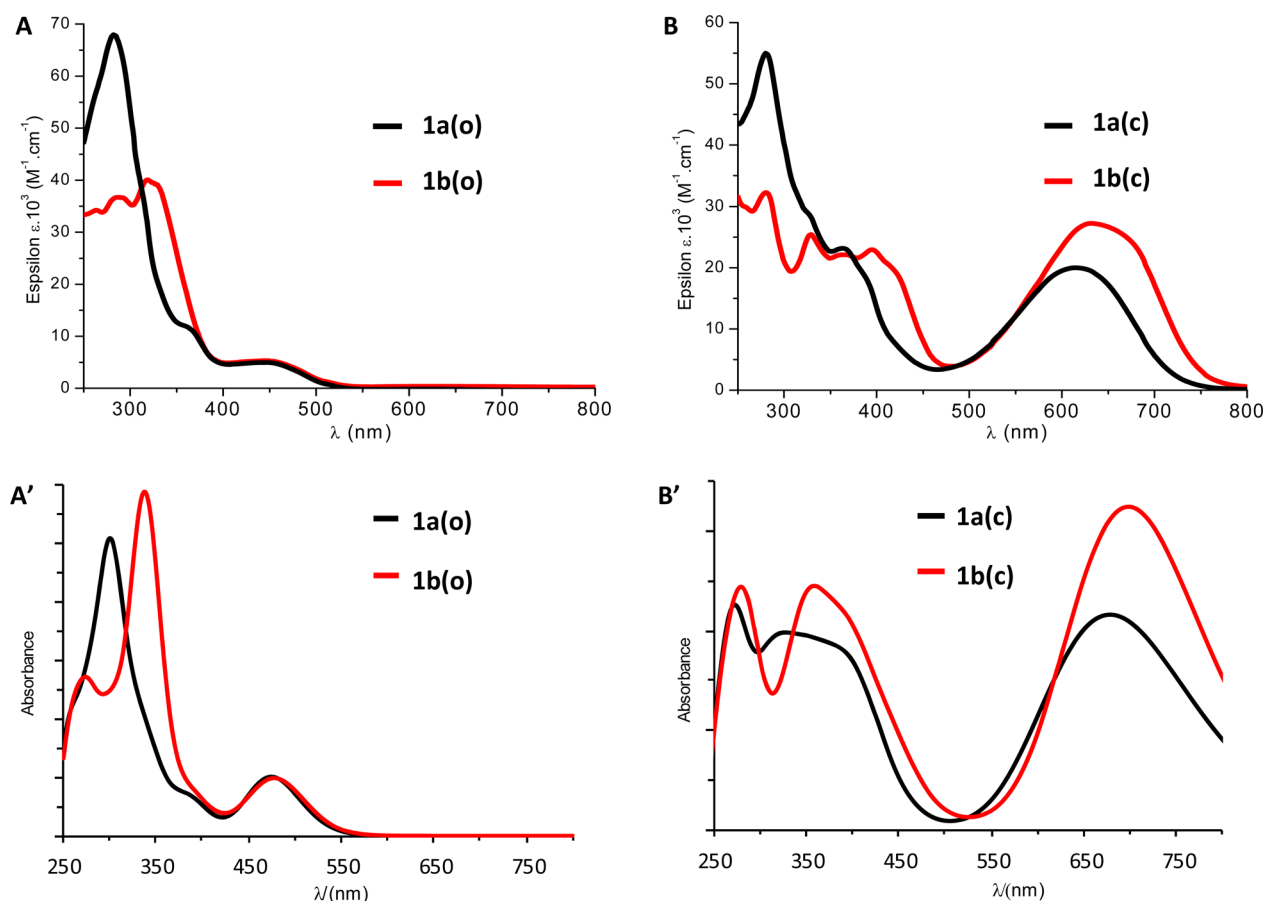


Figure 2. (Top) UV-vis absorption spectra of **1a** and **1b** in their (A) open (o) and (B) closed (c) (PSS) forms. (Bottom) TD-DFT-computed UV-vis spectra of **1a** and **1b** in their (A') open (o) and (B') closed (c) forms.

Table 1. Absorption Data for **1a,b in Their Open and Closed (PSS) Forms Measured in CH₂Cl₂**

complex	λ_{abs}^a [nm] ($\epsilon \times 10^3$ [dm ³ mol ⁻¹ cm ⁻¹]), open form	λ_{abs}^a [nm], closed form (PSS) ^b
1a	365 (11.5), 450 (4.9)	365, 385, 388sh, 616
1b	325 (38.8), 450 (4.9)	329, 365, 395, 422sh, 633

^aAt 298 K in 2.5×10^{-5} M. ^bPSS = photostationary state; 95% ring closing determined by ¹H NMR spectroscopy.

calculations have been performed to simulate the UV-vis spectra in solution (CH₂Cl₂) of complexes **1a,b** in their open and closed forms. The calculated absorption wavelengths for the studied complexes are reported in Table 2. The simulated

Table 2. Computed Absorption Wavelengths at the PCM-PBE0/LANL2DZP Level in CH₂Cl₂

compound	λ_{max} (nm)	oscillator strength (<i>f</i>)	main transition (weight)
1a(o)	385	0.12	HOMO → LUMO+2 (+91%)
	476	0.27	HOMO → LUMO (+97%)
1a(c)	317	0.28	HOMO-7 → LUMO (+80%)
	680	0.79	HOMO → LUMO (+99%)
1b(o)	340	1.06	HOMO → LUMO+4 (+88%)
	481	0.25	HOMO-1 → LUMO (+69%)
1b(c)	378	0.42	HOMO-3 → LUMO (+67%)
	699	1.04	HOMO → LUMO (+98%)

electronic spectra are displayed in Figure 2 (bottom: Figure 2A' and 2B'), and the molecular orbitals (MO) involved in the relevant electronic transitions are shown in Figure S2 (see Supporting Information).

TD-DFT results confirm the assignments given above for the different absorption bands. The lowest energy absorption band of **1a(o)** and **1b(o)** in their open forms is computed at 476 and 481 nm, corresponding mainly to a HOMO → LUMO and HOMO-1 → LUMO transition, respectively. This band can be assigned as L'LCT/MLCT transitions, the HOMO being delocalized on the platinum and the acetylide-thienyl fragment with a weight of 12% (13%) for the metal atom, whereas the LUMO is located on the bipyridine of the cyclometalated ligand (see Figure S2, Supporting Information). In agreement with the experimental data and chemical intuition, this absorption band is similar for both derivatives (D = H, NMe₂). A moderate to intense band in the UV region in the spectrum of **1a(o)** (**1b(o)**) is computed at 385 nm (340 nm). Experimentally, photocyclization can be triggered by irradiation at 350 nm for both complexes. For **1a**, this process involves a HOMO → LUMO+2 electronic transition from a transition assigned as IL'CT/ML'CT transitions involving the alkynylthienyl fragment (left part of L' vs C₅F₆). By contrast, the high-energy band of **1b** results from a HOMO → LUMO+4 transition, attributed to an IL'($\pi \rightarrow \pi^*$) transition that involves the (aminophenyl)thiophene group (right part of the open DTE-based ligand L') as a result of the presence of a terminal electron-donating group. The LUMO+2 of **1a** and LUMO+4 of **1b** exhibit a significant density on the reactive carbons atoms

Table 3. $\mu\beta_{\text{EFISH}}$ and β_{EFISH} of the Investigated Pt(II) Complexes **1a**, **b** in Their Open and Closed (PSS) Forms

complex	$\mu\beta_{\text{EFISH}}^{a,b}$ open	$\mu\beta_{\text{EFISH}}^{a,b}$ closed (PSS)	$\mu,^c$ open	$\mu,^c$ closed	$\beta_{\text{EFISH}}^{d,e}$ open	$\beta_{\text{EFISH}}^{d,e}$ closed (PSS)
1a	−180	−1150	15.70	18.71	−11	−61
1b	−220	−2635	11.30	12.31	−19	−214

^aMeasured in CH₂Cl₂ at a concentration of 10^{−3} M; estimated uncertainty in EFISH measurements is $\pm 10\%$. ^b10^{−48} esu. ^cDFT-calculated dipole moments. ^dValues obtained using DFT-calculated dipole moments. ^e10^{−30} esu.

and the required bonding character of the interacting orbitals for the ring-closure reaction (Figure S2, Supporting Information), the so-called photochromic shape.²⁶ The two reactive carbons of these LUMOs present a weight of 8.05%, 13.70% for **1a** (LUMO) and 2.90%, 16.60% for **1b** (LUMO+2), respectively. Therefore, electrocyclization could process directly from the excited states corresponding to these UV bands, though relaxation to a lower triplet MLCT state followed by cyclization could also be an effective process.

Let us now turn to the closed forms: the absorption bands in the visible region of **1a**(c) and **1b**(c) are computed at 680 and 699 nm, respectively. The red shift experimentally observed (17 nm) is well reproduced, illustrating the influence of the terminal end donor group. The corresponding excitation induces the reopening process; experimentally, cycloreversion is triggered upon irradiation at 650 nm. From Figure S2, Supporting Information, it can be seen that this excitation corresponds to promotion of an electron from the HOMO delocalized along the π -conjugated acetylide ligand (L') containing the closed DTE fragment to the LUMO delocalized over the entire molecule, assigned to a blend of IL'($\pi \rightarrow \pi^*$) and L'LCT transitions. Moreover, the LUMOs of both molecules are suitable for the ring-opening process; they are characterized by an antibonding interaction between the two carbons to be separated, the Mulliken overlap population between them presenting a negative value equal to −0.015 (−0.009) *e* for **1a** (**1b**). A net decrease of the platinum contribution to the HOMO is found for the two closed forms compared to that of the open isomers, with a weight of 3% (2%) for **1a** (**1b**). The UV absorption band is calculated at 317 nm (378 nm), which originates from a HOMO-7 \rightarrow LUMO (HOMO-3 \rightarrow LUMO) transition assigned to L'LCT/IL' excitations.

Quadratic NLO Studies. In order to investigate the second-order NLO properties of the Pt(II) complexes **1a**, **b**, the EFISH method²¹ has been used (see Supporting Information) as it can provide direct information on the intrinsic dipolar molecular second-order NLO properties through

$$\gamma_{\text{EFISH}} = (\mu\beta_{\text{EFISH}}/SkT) + \gamma(-2\omega; \omega, \omega, 0) \quad (1)$$

where $\mu\beta_{\text{EFISH}}/SkT$ is the dipolar orientational contribution and $\gamma(-2\omega; \omega, \omega, 0)$, a third-order term at frequency ω of the incident light, is a purely electronic cubic contribution which can usually be neglected when studying the second-order NLO properties of strongly dipolar molecules.¹ The $\mu\beta_{\text{EFISH}}$ values were measured in CH₂Cl₂ solution (concentration = 10^{−3} M) working with a nonresonant incident wavelength of 1.907 μm . To obtain β_{EFISH} , the projection along the dipole moment axis of the vectorial component of the tensor of the quadratic hyperpolarizability, it is necessary to know the dipole moment, μ . In the present study we used the DFT-computed dipole moments (Table 3; Table S5 and Figure S4, Supporting Information). The values of $\mu\beta_{\text{EFISH}}$ as well as the corresponding β_{EFISH} , before and after UV irradiation, are

reported in Table 3. Like the cyclometalated Pt(II) complexes (C^N)Pt(acac)^{13a,b} and (N^C^N)Pt(X),^{13c} both complexes **1a** and **1b** are characterized by a negative value of $\mu\beta_{\text{EFISH}}$, irrespective of the form of the DTE unit (open or closed), in agreement with a negative value of $\Delta\mu_{\text{eg}}$ (difference between the dipole moments of the excited and ground states). This behavior can be attributed to a quadratic NLO response dominated by a CT from the Pt–acetylide DTE moiety to the cyclometalated ligand. Such CT character appears clearly in the S₁–S₀ density differences plots computed with TD-DFT (see Figure S3, Supporting Information).

As evidenced in Table 3, the absolute values of $\mu\beta_{\text{EFISH}}$ and β_{EFISH} of the two Pt(II) complexes in their open forms are very weak, in the same range of those already reported for DTE-based bipyridine metal complexes in the same form.^{7–9} A dramatic increase of the second-order NLO activity is observed after UV irradiation and subsequent accumulation of the ring-closed isomers: in the case of **1a** the β_{EFISH} value is increased almost 6-fold, while a 12-fold enhancement is observed for **1b**. The large enhancement of the quadratic NLO response upon ring closing clearly reflects the delocalization of the π -electron system in the closed forms, accompanied by an important decrease of the HOMO–LUMO gap (Table S2, Supporting Information), the largest NLO enhancement being observed for the complex featuring the electron-donor dimethylamino end group. Although the ground-state dipole moment of the closed form of **1b** is lower than that of **1a**, its $\mu\beta_{\text{EFISH}}$ value is more than 2-fold enhanced. The 3.5 times larger β_{EFISH} of **1b** (PSS) vs **1a** (PSS) can be due to a greater charge transfer distance (d^{CT} multiplied by a factor of 2.6; see Table S2, Supporting Information) and therefore to a larger $\Delta\mu_{\text{eg}}$.

We found it interesting to carry out computations of the first hyperpolarizabilities of the considered species using the $\omega\text{B97X/LANL2DZP}$ level of theory. The ωB97X functional presents a correct asymptotic behavior (exact exchange going to 100% when the electron separation goes to infinity), and this is known to be a requirement for accurate NLO properties. On the other hand, we remind that for electronic spectra PBE0 is known to be one of the best compromises, at least within the vertical approximation (see the Supporting Information for more details). The obtained total static β_{Stat} and dynamic β_{Dyn} first hyperpolarizabilities, computed at the $\omega\text{B97X/LANL2DZP}$ level of theory, are listed in Table S3, Supporting Information. The theoretical results, in agreement with the experimental ones, reproduce very well the important increase of the NLO response when going from open to closed forms of the complexes and when going from **1a** (c) to **1b** (c).

To study the second-order NLO properties of the Pt(II) complexes **1a** and **1b** in the solid state, we prepared thin films of the chromophores dispersed in a polymethylmethacrylate (PMMA) matrix as reported in the Experimental Section. The complexes were deposited in the closed form, due to a higher dipole moment in the closed than in the open form (Table 3), in a way to optimize the orientation of the chromophores during the poling. UV–vis absorption spectra of the complex

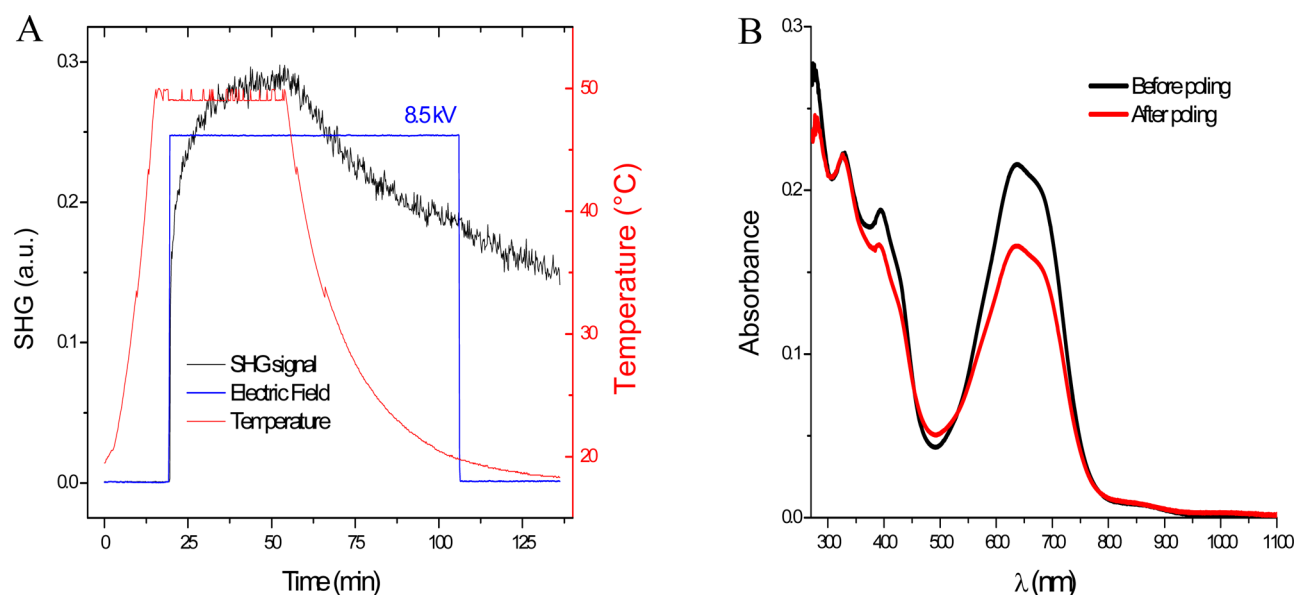


Figure 3. Thin film of the complex **1b** in closed form (PSS): (A) Poling experiment; (B) UV-vis absorption spectra before and after poling.

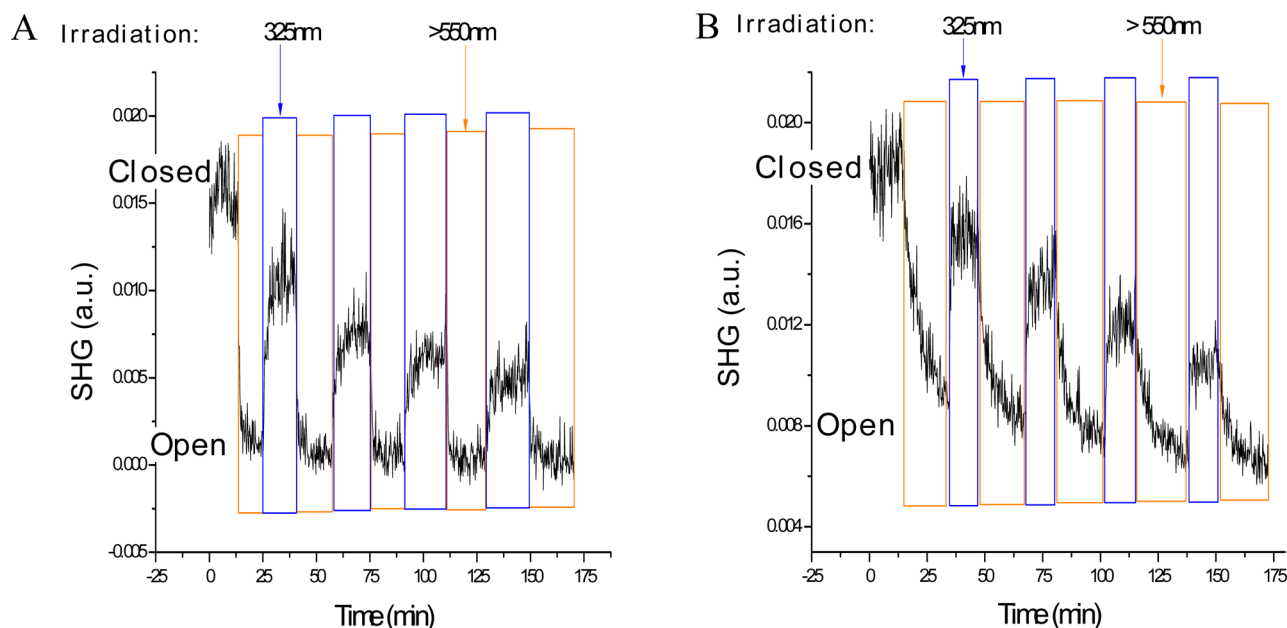


Figure 4. Photoswitch of the poled thin film: (A) complex **1a** and (B) complex **1b**.

1a(c) and **1b(c)** films before poling are illustrated in Figure S5B, Supporting Information, and Figure 3B, respectively. Since they show absorption bands very similar to that reported for the same complex in solution (Figure 2B), one can consider the molecules of complexes **1a(c)** and **1b(c)** inside the films as isolated and only weakly interacting with the polymer matrix.

The poling measurement of the complex **1b(c)** film is shown in Figure 3A, in which the optimized poling parameter temperature (50 °C) and electric field (8.5 kV) have permitted us to obtain a sufficiently high and stable second-harmonic generation (SHG) signal. The UV-vis absorption spectrum of the complex **1b(c)** film after poling is illustrated in Figure 3B; the decrease of the absorption band (at peak 637 nm) compared to that observed before poling (so-called dichroic effect) is due to the partial orientation of molecules along the direction of the electric poling field.²⁷ No appreciable Stark

shift²⁷ of the absorption peaks was noted after poling. A very similar behavior is observed for the poled complex **1a(c)** film (Figures S5A and S5B, Supporting Information), although we point out a lower SHG signal after poling.

Figure S6, Supporting Information, presents Maker fringes measurements for the films based on complexes **1a** and **1b** in closed and open forms. These measurements have been performed after poling for the closed form while after poling and irradiation at $\lambda > 550$ nm (at least 30 min) for the open form. We note that 30 min is a sufficient irradiation time to reach the photostationary state of the open form for complex **1a** film (see, for example, the first photoswitch in Figure 4A), whereas this irradiation time is not sufficient to convert completely the chromophores from closed to open form for the complex **1b** film (Figure 4B). In particular, in the latter case we

observed that the photostationary state is not reached even after a much longer time (3 h).

The standard expression²⁸ used to fit the SHG intensity in a Maker fringe measurement includes the absorption coefficient of the film at the harmonic frequency. In this expression the SHG intensity is proportional to the square of the effective nonlinear optical coefficient (d_{eff}) that depends on polarizations of the fundamental and SH beam. Considering the $C_{\infty v}$ symmetry expected for poled films and the polarizations of the fundamental and SH beam, the coefficient d_{eff} assumes the expression

$$d_{\text{eff}} = d_{31} \sin \theta_2$$

for s \rightarrow p configuration (2a)

$$d_{\text{eff}} = d_{15} \sin \theta_1$$

for 45 \rightarrow s configuration (2b)

$$d_{\text{eff}} = 2d_{15} \sin \theta_1 \cos \theta_1 \cos \theta_2 + \sin \theta_2 (d_{31} \cos^2 \theta_1 + d_{33} \sin^2 \theta_1)$$

for p \rightarrow p configuration (2c)

where θ_1 and θ_2 are, respectively, the angles of refraction inside the poled film for the fundamental and SH beam with refractive indices n_{ω} and $n_{2\omega}$ ($\sin \theta_m = \sin \theta / n_{m\omega}$, $m = 1, 2$). It is worthwhile remembering that the components of the nonlinear optics coefficient and the susceptibility tensor are related by the formula $2d_{ij} = \chi_{ij}^{(2)}$.

By fitting the Maker fringe measurements using these expressions (eqs 2a–2c) the three nonzero coefficients of the second-order susceptibility tensor for a poled film $\chi_{33}^{(2)}$, $\chi_{31}^{(2)}$, and $\chi_{15}^{(2)}$ have been evaluated (Table 4); the error in these data

Table 4. Susceptibility Components of Poled Films Complexes 1a,b in Closed Form and Switched Open Form upon Irradiation at $\lambda > 550$ nm

complex	$\chi_{33}^{(2)}$ (10^{-10} esu)	$\chi_{31}^{(2)}$ (10^{-10} esu)	$\chi_{15}^{(2)}$ (10^{-10} esu)	$\chi_{33}^{(2)}/\chi_{31}^{(2)}$	$\chi_{33}^{(2)}/\chi_{15}^{(2)}$
1a(c)	7.64	4.77	1.95	1.60	3.91
1a(o)	3.87	2.39	1.67	1.32	2.31
1b(c)	16.80	16.71	3.10	1.01	5.41
1b(o) ^a	13.84	9.55	2.86	1.45	4.84

^aNote: 1b(o) has not reached the photostationary state of the open form.

can be estimated to be less than 20%. As shown in Table 4, for both 1a and 1b the $\chi_{33}^{(2)}$, $\chi_{31}^{(2)}$, and $\chi_{15}^{(2)}$ values increase going from the open to the closed form and the largest NLO enhancement is observed for the complex featuring the strong electron-donor dimethylamino end group, confirming what has been seen in the EFISH measurements. Moreover, the $\chi_{33}^{(2)}/\chi_{31}^{(2)}$ and $\chi_{33}^{(2)}/\chi_{15}^{(2)}$ ratios are not close to 3, the expected value in a poled film containing chromophores having a one-dimensional first hyperpolarizability tensor.²⁹ This behavior of the second-order susceptibility tensor, particularly emphasized for the film based on complex 1b(c) in which $\chi_{31}^{(2)}$ is about equal to $\chi_{33}^{(2)}$, suggests that the charge transfer inside the chromophore is not only in the direction of the dipole moment but that other contributions are present in other directions,^{22,30} in agreement with our theoretical data (see Figures S3 and S4, Supporting Information).

From an application point of view, an interesting aspect of metal complexes is the possibility to switch their NLO response.^{2,4,30,31} The good second-order NLO properties of the polymeric films based on the Pt(II) complexes 1a and 1b prompted us to investigate the switching of the NLO response in the solid state. SHG photoswitching experiments have been performed after poling for complex 1a,b films in closed form (see Figure 3): the SHG signal increases after UV irradiation, as the closed form was generated from the open one. Once a stable plateau is reached, UV irradiation was stopped and visible light was turned on. The SHG intensity decreased as the closed form converted back to the open form. The first photoswitch presents a contrast of about 80% and 50% for complexes 1a and 1b, respectively (Figure 4A and 4B). For complex 1b, the lower contrast could be attributed, at least in part, to the not complete conversion of the chromophores from the closed to the open form. In any case, the observed NLO contrasts exceed those recently reported for “all organic” phenyl-substituted DTE thin films.²² A feature common to both measures is the loss of some SHG signal during the switches, due to the irreversible loss of orientation through the photoisomerization processes. This behavior has already been observed in PMMA³² and could be reduced in the near future, for example, using a cross-linking technique for preparation of the polymer film.

As noted above, complexes 1a and 1b have a different photoisomerization time to reach the PSS. For complex 1b, conversion from the closed to the open form is slow and not completed even after 3 h while the reverse conversion is very fast (see Figure 4B); instead, an opposite behavior is observed for complex 1a (see Figure 4A) with a fast conversion from the closed to the open form (less than 30 min) and a relatively slow reverse conversion. Such a behavior has been already observed in solution for photochromic bipyridine ligands and Zn complexes.^{7b}

CONCLUSIONS

The new cyclometalated ($C^{\wedge}N^{\wedge}N$)Pt($C\equiv C$ –DTE– C_6H_4 –D) complexes investigated in the present work are a new family of organometallic second-order NLO chromophores with a response easily tunable by a rational approach, where the Pt atom plays the role of a central bridge of the transfer process from the donor to the acceptor moieties of the molecular structure. Remarkably, use of a strong electron-donor group (D = NMe₂) leads to the best $\mu\beta_{\text{EFISH}}$ reported up to now for a Pt(II) complex. Moreover, their excellent photochromic properties allow photoinduced switching of their second-order nonlinear optical properties.

The presence of *n*-hexyl substituents on the cyclometalated ligand is a tool for their straightforward nanoorganization in polymer films which can be easily poled affording new materials characterized by a good second-order NLO response that can be easily switched, with an excellent NLO contrast, by interaction with electromagnetic radiation.

To our knowledge, this study represents the first demonstration of the photomodulation of the NLO response of a photochromic metal complex in thin films, opening a new avenue for preparation of convenient reversible-NLO switches.

ASSOCIATED CONTENT

Supporting Information

Description of the synthesis, characterization, and photoisomerization of the new compounds in solution, EFISH and Maker fringe measurements, and computational details. This

material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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