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# Intriguing Second-Order NLO Switches Based on New DTE Compounds

Julien Boixel,*[a] Alessia Colombo,[b] Francesco Fagnani,[b] Paola Matozzo,[b] and Claudia Dragonetti*[b]

Two new photochromic compounds bearing a dithienylethene unit have been designed, synthesized, and well characterized. The first contains a platinum dialkynyl moiety whereas the second bears a simple phenyl-dimethylamino fragment. Both compounds have demonstrated an excellent photochromic behavior. This efficient photochromism is the springboard for a significant photomodulation of the second-order nonlinear optical properties, determined in dichloromethane solution by means of the Electric Field Induced Second Harmonic generation technique. The results are of interest for the design of reversible NLO switches as a tool for emerging photonic technologies.

## Introduction

The modulation of the optical properties of molecules by an exterior stimulus has deeply fascinated scientists in the last fifteen years. As a matter of fact, the introduction of a molecular switch into a material is an elegant way to control their optical properties and is of interest for photonic communication and data processing.[1] Thus, research on the modulation of the second-order nonlinear optical (NLO) properties of molecules has gained increasing interest.[2]

It is known that intense second-order NLO responses of molecules are mainly due to the presence of π-extended systems and charge-transfer transitions. The archetype can be described with an electron-donor fragment (D) connected to an electron-acceptor fragment (A) through a π-conjugated bridge.[3] In particular, coordination complexes are interesting candidates due to their versatile charge transfer transitions, involving the metal (acting as donor or acceptor or bridge) and the ligands. They are characterized by intense and low-energy intra-ligand (ILCT), ligand-to-metal (LMCT), and metal-to-ligand (MLCT) charge transfer transitions, that can be tuned by the nature of the metal and the ligands.[4]

The on/off second-order NLO switching can be caused by a reduction of the donor strength of D upon protonation or oxidation, whereas the acceptor behavior of A can be modified by deprotonation or reduction. Manipulation of the NLO properties can also be reached through modification of the bridge, thus modifying the communication between D and A. Accordingly, NLO switches can be realized by pH variation, by a redox reaction, or by interaction with an electromagnetic radiation. Moreover, the use of light to control the second-order NLO properties of molecules is fascinating because it leads to all-optical molecular materials, where light is used to read, write, and store the information.[5] In this context, dithienylethenes (DTEs) are useful photochromic molecular switches because they are characterized by a good thermal stability, a high photoconversion, and very different optical behaviors of its open (o) and closed (c) isomers.[6] The photochromic reaction between the open and the closed isomers, induces a change in the π-delocalization over the DTE backbone.[7] Because multiple reversible photoswitching cycles can be achieved without degradation; DTEs have been successfully employed in various fields such as photoresponsive optoelectronic and probes.[2h,i] For example, some of us reported the photoswitch of both the luminescent and the second-order NLO properties in DTE-based platinum complexes.[8] Two photochromic dithienylethene-based platinum(II) complexes (C^N^N)Pt(C≡C-DTE-$C_6H_4$-D) ((C^N^N) = 4,4′-di(n-hexyl)-6-phenyl-2,2′-bipyridine; D = H, $NMe_2$) were reported,[8a] their excellent photochromic properties allow the photoinduced switching of their second-order nonlinear optical properties in solution, leading to a large increase (from 6 to 12 times) of the negative $\mu\beta_{EFISH}$ of the chromophores. A different approach has been reported[8b] for a DTE-based platinum complex with the organometallic fragment and the dialkylaminophenyl group located on the same thiophene ring of the photochromic DTE unit, the cyclometalated Pt(II) acetylide moiety being bounded to one of the reactive carbon atoms. In that case there is an *in situ* sequential double nonlinear optical switch where the NLO response is modulated first by protonation and then upon irradiation with UV light. One key point of the system is that the sign of the μβ response changes at each step.[8b] Among the few examples, to our knowledge, of second-order NLO active Pt-DTE complexes,

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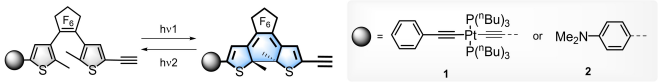
there is a theoretical work[8c] that should be mentioned. It turned out that the computed quadratic hyperpolarizability of a simple dichloride Pt dithienyl compound increases by a factor of 5.4 on going from the open to the close form in agreement with an increase of the system delocalization. In the related bimetallic platinum complex, a similar trend is observed although the quadratic hyperpolarizabilities are lower. Interestingly, substitution of the cyclopentene ring with a perfluorocyclopentene causes a decrease of the second-order NLO response. These results confirm that the introduction of a DTE moiety is an effective method to allow switching of the quadratic hyperpolarizability. [8c]

Overall, it appeared that Pt(II) dialkynyl complexes are characterized by excellent second-order NLO properties.[2h,9] This observation and the interesting properties of dithienylethenes prompted us to synthesize a new Pt(II) dialkynyl complex (photochrome **1**) and, for comparison, a new organic chromophore (photochrome **2**) both bearing a DTE unit (Scheme 1). In the first case (**1**), the DTE unit is linked through a triple bond to platinum whereas in the second case (**2**), DTE is directly linked to the aromatic ring of a phenyl-*p*-$NMe_2$ fragment.

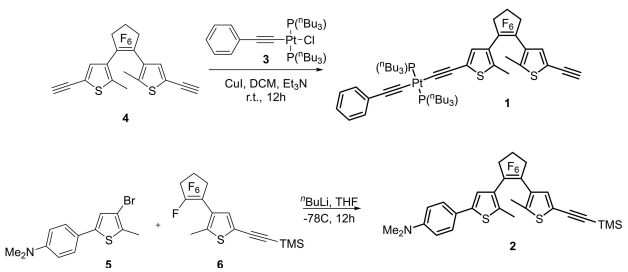
## Results and Discussion

The preparation of photochromes **1** and **2** is shown in Scheme 2. Both synthetic routes start from the functionalization of the 2,4-dibromo-5-methylthiophene with trimethylsilylacetylene (TMSA) to give compound 7; then, reaction with perfluorocyclopentene in the presence of butyllithium gives statistically the mono- and bi-nucleophilic substitution affording compound **6** and DTE **5**, respectively. After removing the protecting silyl groups, DTE **4**[7,10] is engaged in Sonogashira-like reaction with the known platinum chloride precursor (compound 3),[9a,11] to give the target complex **1**. Compound **6** is coupled with the amino-functionalized thiophene **8**, also prepared from the 2,4-dibromo-5-methylthiophene, to afford the wanted DTE photochrome **2**.[8a] Both target compounds **1** and **2** are isolated in their open forms and fully characterized by means of $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectroscopies and elemental analysis (see details in S.I.).

The steady-state absorption spectra of compounds **1** and **2** in dichloromethane solution ($C \approx 10^{-5}$ M) are presented in Figure 1 and Figure 2, respectively, and the data are summarized in Table 1.




**Scheme 1.** Chemical structures of the investigated photochromic compounds **1** and **2**.




**Scheme 2.** Synthetic routes for compounds **1** and **2**.

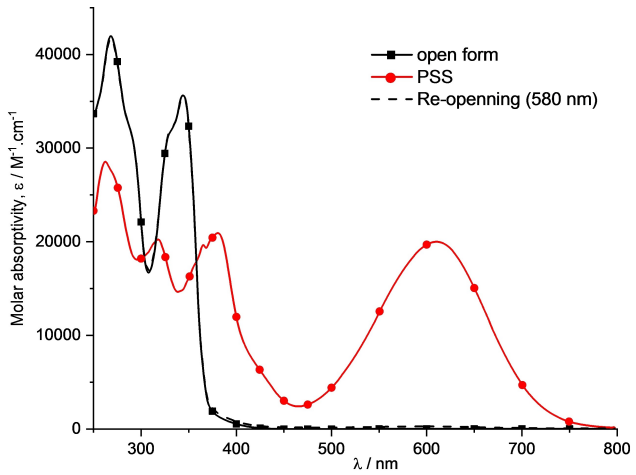



**Figure 1.** UV-Visible absorption spectra of **1** in $CH_2Cl_2$, in the open form (black squares) and upon irradiation at 350 nm (PSS, red circles).

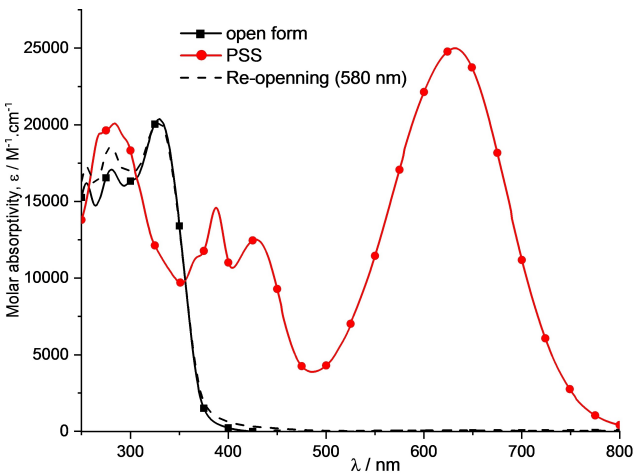



**Figure 2.** UV-Visible absorption spectra of **2** in $CH_2Cl_2$, in the open form (black squares) and upon irradiation at 350 nm (PSS, red circles).

**Table 1.** UV-vis absorption data of the investigated complexes.

| | $\lambda_{abs}$[a]/nm (ε $10^{-4}$/$M^{-1}cm^{-1}$) Open *(o)* forms | $\lambda_{abs}$[a,b] [nm] Closed *(c)* forms (PSS) |
|---|---|---|
| **1** | 268 (41.8), 290sh (31.3), 330sh (31.6), 344 (35.6) | 262, 318, 380, 424sh, 610 |
| **2** | 281 (16.8), 302sh (16.4), 329 (20.4) | 283, 297sh, 366sh, 387, 428, 631 |

[a] Measured in $CH_2Cl_2$ solution at 298 K. [b] After irradiation at 350 nm.



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The electronic absorption spectrum of complex **1**(o), in its open form, exhibits two sets of absorption bands in the UV region centered at 270 and 340 nm, originated from intra-ligand IL(π–π*) transitions. Additional band at lower-energy, tailing up to 420 nm, is attributed to charge transfer transition evolving the alkynyl platinum moiety.[6b] The DTE **2**(o) also shows mainly IL(π–π*) transition in the UV region (λmax = 320 nm). The electron-donating dimethylamino end group produces lower-lying IL transition up to 410 nm.[8a]

The photochromic reaction of **1** and **2** are monitored by UV-visible absorption upon 350 and 580 nm light irradiations for photo-cyclization and -cycloreversion, respectively. For both compounds, the initial slight yellow solutions turn dark blue upon 350 nm exposure due to the appearance of the broad visible absorption band of the closed DTE moiety, originated of IL(π–π*). The λmax of the broad visible absorption is red-shifted of about 20 nm in **2** compared to **1**, as expected for the strongest electron-donating ability of the *p*-dimethylamino benzene with respect to the alkynyl platinum part. Monitoring the ring-closure reaction by $^1$H NMR spectroscopy gives access to the percentage of conversion at the photostationary state (PSS).

Figure S1 (see SI) shows the $^1$H NMR spectral changes of **1** upon irradiation at 350 nm. Characteristic $^1$H NMR signal shifts are observed with upfield shifted singlets (from 7.26 to 6.43 ppm and from 6.77 to 6.03 ppm) assigned to the thienyl protons on the DTE core, together with downfield shifted singlets (from 1.93 and 1.82 to 2.13 and 2.10 ppm, respectively) corresponding to the methyl protons. The relative integration of the above thienyl signals between the open and the closed form of 1 reveals a photoconversion at the PSS of 75% in closed form. (see Table 1 and Figure S1).

The second-order NLO properties in solution of compounds **1** and **2** have been investigated by the Electric Field Induced Second Harmonic generation (EFISH) technique that provides direct information on the intrinsic molecular NLO properties through the following equation:[12]

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

where $\mu\beta_{EFISH}$/5kT 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 to $\gamma_{EFISH}$ which can usually be neglected when studying the second-order NLO properties of dipolar compounds.

EFISH measurements were carried out in dichloromethane solutions at a concentration of $10^{-3}$ M, with a non-resonant incident wavelength of 1.907 μm, obtained by Raman-shifting the fundamental 1.064 μm wavelength produced by a Q-switched, mode locked $Nd^{3+}$:YAG laser. The second-order NLO responses were determined both on the open and on the closed form of compounds **1** and **2** (see Table 2).

EFISH values can be either positive or negative. What is relevant is the absolute value of $\mu\beta_{EFISH}$, in fact a chromophore is a good second order NLO-phore if its absolute value of $\mu\beta_{EFISH}$ is as high as possible. If a MLCT transition dominates β the $\mu\beta_{EFISH}$ value is negative, otherwise if an ILCT transition dominates β the $\mu\beta_{EFISH}$ value is positive.[2,3]

**Table 2.** EFISH measurements of the investigated compounds.

| Compound | $\mu\beta_{EFISH}$ ($\times 10^{-48}$ esu) |
|---|---|
| **1-open** | $-367 \pm 33$ |
| **1-closed** | $-1032 \pm 108$ |
| **2-open** | $35 \pm 4.8$ |
| **2-closed** | $147 \pm 15$ |

As expected for a higher π-delocalization and a lower HOMO-LUMO gap, the closed form in both cases has a $\mu\beta_{EFISH}$ value higher than the open one, in fact a dramatic increase of the second-order NLO activity is observed after UV irradiation and subsequent accumulation of the ring closed isomers. Compound **1**, containing the platinum center, has negative values of $\mu\beta_{EFISH}$, suggesting a diminution of the dipole moment upon excitation.[13] This behavior is in agreement with that of other Pt(II) complexes[2h,8] where MLCT transitions dominate the quadratic hyperpolarizability. The $\mu\beta_{EFISH}$ value of the closed form of **1** is about three times the one of the open form, a contrast similar to that observed for a photochromic Pt(II) compound with a cyclometalated dipyridylbenzene in which the DTE unit is linked to the phenyl ring of the N^C^N ligand.[2h] A better contrast was reported for a photochromic Pt(II) complex with a cyclometalated phenylbipyridine in which DTE is directly linked to Pt through a triple bond[8a] putting in evidence that a Pt(N^N^C) moiety behaves as a stronger acceptor than a $PhCCPt(PBu_3)_2$ fragment. Compound **2**, without the platinum metal, has positive values of $\mu\beta_{EFISH}$, in agreement with an increase of the dipole moment upon excitation, the value of the closed form being about four times that corresponding to the open form.

Remarkably, the absolute $\mu\beta_{EFISH}$ values of complex **1**, with the Pt center, are higher both in the open and in the closed form with respect to compound **2**, underlining the importance of the metal in the second order nonlinear optical response of this class of compounds.

## Conclusion

In summary, two new photochromic compounds containing a photochromic DTE unit have been designed and easily synthesized. Both compounds have demonstrated an excellent photochromic behavior upon UV or visible light irradiation. Remarkably, this efficient photochromism leads to a significant NLO photomodulation of the second order response of the two compounds in dichloromethane solution, a behavior particularly appealing for the design of reversible NLO switches for emerging photonic technologies. The next step will be the nanoorganization of the photochromes in polymeric films with the aim of obtaining, after poling, new materials with a good second-order NLO response that could be easily switched, with a useful NLO contrast



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## Experimental Section

### General

All syntheses were performed using Schlenk techniques under argon atmosphere. All solvents were dried and purified by standard procedures. Precursor **3**[1], **4**[2], **5**[3] and **6**[3] were synthesized according to the reported procedure. NMR spectra were recorded on Bruker, Avance III spectrometer. $^{1}H$, $^{19}F$, $^{13}C$ and $^{31}P$ chemical shifts are determined by reference to residual solvent signals.

**Photochromism followed by UV-visible absorption**: Complex **1** and DTE **2** were irradiated in dichloromethane solution ($C \approx 10^{-6}$ M) with a light source of ABET technologies, Inc (150 W xenon lamp), with single wavelength light filters "350FS 10-25" or "450FS 40-25" for ring-closure and "650FS 10-25" for cycloreversion.

**Photochromism followed by proton NMR spectroscopy**: Complex **1** and DTE **2** were irradiated in $CD_2Cl_2$ solution ($C \approx$ 10-3 M), using a Rayonet® with 350 nm light emitting lamps.

### Syntheses

**Synthesis of 1**: Compound **3** (240 mg, 0.4 mmol) was dissolved in 10 mL of dried $Et_2NH$ under Ar. **4** (300 mg, 0.4 mmol) was injected. Then the mixture was stirred under Ar at 45 °C for 8 h. After the reaction was finished, the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, $CH_2Cl_2$/pentane = 1:5, v/v). **1** was isolated as a yellow powder (200 mg, 42%). **$^{1}$H-NMR (400 MHz, $CD_2Cl_2$)**: 7.26–7.17 (m, 5H, Ar + thio), 7.12–7.09 (m, 1H, Ar), 6.77 (s, 1H, thio), 2.10–2.07 (m, 12H, nBu), 1.92 (s, 3H, Me), 1.81 (s, 3H, Me), 1.63–1.56 (m, 12H, nBu), 1.50–1.41 (m, 12H, nBu), 0.93 (t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 18H, nBu). **$^{19}$F-NMR (376.5 MHz, $CD_2Cl_2$)**: −110.36, −110.72, −132.27 (t, $^{3}J_{F\text{-}F}$ = 5.1 Hz). **$^{31}$P-NMR (162 MHz, $CD_2Cl_2$)**: 3.48 (t, $^{2}J_{H\text{-}P}$ = 1168 Hz).

**Synthesis of 2**: Compound **5** (1.07 g, 3.62 mol) was dissolved in 12 mL of dried THF and cooled at −78 °C under argon. $^{n}$BuLi (1 M in THF: 1.73 mL, 3.98 mol) was added dropwise and the reaction mixture was stirred at −78 °C for 30 min. A solution of **6** (1.40 g, 3.62 mol) in dry THF (12 mL) was added dropwise by cannula at −78 °C. The reaction mixture was stirred overnight and allowed to warm at room temperature. The crude was purified by column chromatography (silica gel, $CH_2Cl_2$/pentane = 3:7, v/v) to afford **2** as green powder (0.675 g, 37%). **$^{1}$H-NMR (400 MHz, $CDCl_3$)**: 7.43 (d, $J$ = 8.9 Hz, 1H, Ar), 7.27 (s, 1H, Hthio), 7.09 (s, 1H, Hthio), 6.74 (d, $J$ = 8.9 Hz, 1H, Ar), 3.01 (s, 6H, $NMe_2$), 1.92 (s, 6H, $CH_3$), 0.28 (s, 9H, TMS). **$^{13}$C-NMR (100 MHz, $CDCl_3$)**: 150.4, 143.6, 143.4, 139.3, 132.4, 126.7, 125.5, 125.1, 121.7, 121.6, 119.8, 112.6, 99.9, 96.6, 40.6, 14.7, 14.6, −0.06.

### EFISH Measurements

EFISH measurements were carried out in dichloromethane solutions at a concentration of $10^{-3}$ M, with a non-resonant incident wavelength of 1.907 μm, obtained by Raman-shifting the fundamental 1.064 μm wavelength produced by a Q-switched, mode locked $Nd^{3+}$:YAG laser manufactured by Atalaser. The reported $\mu\beta_{EFISH}$ values are the mean value of 16 measurements performed on the same sample. EFISH measurements are performed without a standard compound (differently from Kurtz Perry measurements, where a standard is compulsory) The measurement is carried out in the pure solvent and then in solution; the same procedure is repeated for all measurements. The error on EFISH measurements is reported as +/−10′%.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** Dithienylethenes · Nonlinear optics · Photochromism · Photophysics · Platinum

[1] Y. Wang, D. Astruc, A. S. Abd-El-Aziz, *Chem. Soc. Rev.* **2019**, *48*, 558–636.
[2] a) B. J. Coe, *Acc. Chem. Res.* **2006**, *39*, 383–393; b) F. Castet, V. Rodriguez, J.-L. Pozzo, L. Ducasse, A. Plaquet, B. Champagne, *Acc. Chem. Res.* **2013**, *46*, 2656–2665; c) E. C. Harvey, B. L. Feringa, J. G. Vos, W. R. Browne, M. T. Pryce, *Coord. Chem. Rev.* **2015**, *282*, 77–86; d) S. Di Bella, I. P. Oliveri, A. Colombo, C. Dragonetti, S. Righetto, D. Roberto, *Dalton Trans.* **2012**, *41*, 7013–7016 and references therein; e) E. Cariati, C. Dragonetti, E. Lucenti, F. Nisic, S. Righetto, D. Roberto, E. Tordin, *Chem. Commun.* **2014**, *50*, 1608–1610 and references therein; f) F. Nisic, A. Colombo, C. Dragonetti, M. Fontani, D. Marinotto, S. Righetto, D. Roberto, J. A. G. Williams, *J. Mater. Chem. C.* **2015**, *3*, 7421–7427; g) S. Attar, D. Espa, F. Artizzu, L. Pilia, A. Serpe, M. Pizzotti, G. Di Carlo, L. Marchiò, P. Deplano, *Inorg. Chem.* **2017**, *56*, 6763–6767; h) H. Zhao, E. Garoni, T. Roisnel, A. Colombo, C. Dragonetti, D. Marinotto, S. Righetto, D. Roberto, D. Jacquemin, J. Boixel, V. Guerchais, *Inorg. Chem.* **2018** *57*, 7051–7063; i) C.-C. Ko, V. W.-W. Yam, *Acc. Chem. Res.* **2018** *51*, 149–159; j) D. Marinotto, R. Castagna, S. Righetto, C. Dragonetti, A. Colombo, C. Bertarelli, M. Garbugli, G. Lanzani, *J. Phys. Chem. C.* **2011**, *115*, 20425–20432.
[3] a) N. P. Prasad, D. J. Williams, *Introduction to Nonlinear Optical Effects in molecules and Polymers*, Wiley, **1991**; b) J. Zyss, *Molecular Nonlinear Optics: Materials, Physics and Devices*, Academic Press, Boston, **1994**.
[4] a) H. S. Nalwa, *Appl. Organomet. Chem.* **1991**, *5*, 349–377; b) S. R. Marder, in Inorganic Materials, eds. D. W. Bruce, D. O'Hare D, Wiley, New York, **1992**, 115–164; c) N. J. Long, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 21–38; d) I. R. Whittall, A. M. McDonagh, M. G. Humphrey, S. Samoc, *Adv. Organomet. Chem.* **1998**, *42*, 291–362; e) J. Heck, S. Dabek, T. Meyer-Friedrichsen, H. Wong, *Coord. Chem. Rev.* **1999**, *190–192*, 1217–1254; f) H. Le Bozec, T. Renouard, *Eur. J. Inorg. Chem.* **2000**, 229–239; g) C. E. Powel, M. G. Humphrey, *Coord. Chem. Rev.* **2004**, *248*, 725–756; h) S. Di Bella, *Chem. Soc. Rev.* **2001**, *30*, 355–366; i) B. J. Coe, in Comprehensive Coordination Chemistry II; J. A. McCleverty, T. J. Meyer TJ Eds.; Elsevier Pergamon Oxford, U. K., Nonlinear Optical Properties of Metal Complexes, **2004**, *9*, 621–687; j) B. J. Coe, N. R. M. Curati, *Comments on Inorg. Chem.* **2004**, *25*, 147–184; k) O. Maury, H. Le Bozec, *Acc. Chem. Res.* **2005**, *38*, 691–704; l) E. Cariati, M. Pizzotti, D. Roberto, F. Tessore, R. Ugo, *Coord. Chem. Rev.* **2006**, *250*,1210–1233; m) P. Morrall, G. T. Dalton, M. G. Humphrey, M. Samoc, *Adv. Organomet. Chem.* **2007**, *55*, 61–136; n) O. Maury, H. Le Bozec, In Molecular Materials; Eds: D. W. Bruce, D. O'Hare, R. I. Walton, Wiley: Chichester, Meral-based quadratic molecular materials, **2010**, chap 1; o) M. G. Humphrey, T. Schwich, P. J. West, M. P. Cifuentes, M. Samoc, In Comprehensive Inorganic Chemistry II (Second Edition): From Elements to Applications, Elsevier: Oxford, U. K., **2013**, Vol 8; p) A. Colombo, C. Dragonetti, V. Guerchais, C. Hierlinger, E.


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Zysman-Colman, D. Roberto, *Coord. Chem. Rev.* **2020**, *414*, 213293; q) A. Colombo, C. Dragonetti, V. Guerchais, D. Roberto, *Coord. Chem. Rev.* **2021**, *446*, 214113.

[5] V. Guerchais, J. Boixel, H. Le Bozec, Linear and Nonlinear Optical Molecular Switches Based on Photochromic Metal Complexes. In Photon-Working Switches; Yokoyama Y., Nakatani K. Eds.; Springer: Tokyo, **2017** 363–384. .

[6] a) M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716; b) M. Irie, T. Fukaminato, M. Matsuda, S. Kobatake, *Chem. Rev.* **2014**, *114*, 12174–12277.

[7] J. Boixel, Y. Zhu, H. Le Bozec, M. A. Benmensour, A. Boucekkine, K.M–C. Wong, A. Colombo, D. Roberto, V. Guerchais, D. Jacquemin, *Chem. Commun.* **2016**, *52*, 9833–9836.

[8] a) J. Boixel, V. Guerchais, H. Le Bozec, D. Jacquemin, A. Amar, A. Boucekkine, A. Colombo, C. Dragonetti, D. Marinotto, D. Roberto, S. Righetto, R. De Angelis, *J. Am. Chem. Soc.* **2014**, *136*, 5367–5375; b) J. Boixel, V. Guerchais, H. Le Bozec, A. Chantzis, D. Jacquemin, A. Colombo, C. Dragonetti, D. Marinotto, D. Roberto, *Chem. Commun.* **2015**, *71*, 7805–7808; c) Y. Zhang, H.-Q. Wang, J.-T. Ye, X. Li, Y.-Q. Qiu, *J. Organomet. Chem.* **2019**, *888*, 29–36.

[9] a) R. J. Durand, S. Gauthier, S. Achelle, S. Kahlal, J.-Y. Saillard, A. Barsella, L. Wojcik, N. Le Poul, F. Robin-Le Guen, *Dalton Trans.* **2017**, *46*, 3059–3069; b) A. Colombo, F. Nisic, C. Dragonetti, D. Marinotto, I. P. Oliveri, S. Righetto, M. G. Lobello, F. De Angelis, *Chem. Commun.* **2014**, *50*, 7986–7989.

[10] a) A. Osuka, D. Fujikane, H. Shinmori, S. Kobatake, M. Irie, *J. Org. Chem.* **2001**, *66*, 3913–3923; b) Y. Liu, C. M. Ndiaye, C. Lagrost, K. Costuas, S. Chou, P. Turek, L. Norel, S. Rigaut, *Inorg. Chem.* **2014**, *53*, 8172–8188.

[11] W. Yang, A. Karatay, J. Zhao, J. Song, L. Zhao, Y. Xing, C. Zhang, C. He, H. G. Yaglioglu, M. Hayvali, A. Elmali, B. Küçüköz, *Inorg. Chem.* **2015**, *54*, 7492–7505.

[12] a) B. F. Levine, C. G. Bethea, *Appl. Phys. Lett.* **1974**, *24*, 445–447; b) B. F. Levine, C. G. Bethea, *J. Chem. Phys.* **1975**, *63*, 2666–2682; c) I. Ledoux, J. Zyss, *Chem. Phys.* **1982**, *73*, 203–213.

[13] D. R. Kanis, P. G. Lacroix, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10089–10102.

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