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Sequential double-second-order nonlinear optical switch by an acido-
triggered photochromic cyclometallated platinum(II) complex

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An unprecedented DTE-based Pt(II) complex, 2(o), stands as the first example of a sequential double nonlinear optical switch, induced first by protonation and next upon irradiation with UV light.

Among compounds with second-order nonlinear optical (NLO) properties, those with commutable NLO responses are of growing importance due to their potential for novel applications in emerging photonic technologies. For this reason, there is great interest in finding efficient ways to switch the second-order NLO activity at the molecular level. Recently, considerable efforts have been made in designing and preparing coordination complexes with effective redox- or photo-switchable second-order NLO response. For example, by using the photochromic DiThienylEthene (DTE) unit, some of us demonstrated the photo-modulation of the NLO response in several DTE-based bipyridine metal complexes. The ability to switch the NLO response of cyclometallated Pt(II) complexes is appealing, and a density functional theory (DFT) investigation showed that it can be achieved by using well designed DTE ligands. Recently some of us found that the excellent photochromic properties of an open-DTE-based Pt(II) complex (I(o) in Chart 1) allow the photo-induced switching of its second-order NLO properties.

as measured by the Electric-Field-Induced Second Harmonic generation EFISH technique, due to ring closure of the DTE unit and concomitant formation of an extended π-conjugated ligand (I(e)).

Chart 1 Chemical structures of DTE-based (N=N=C)Pt(II) complexes 1, (R = ‘Hex, D = NMe2) and 2 (R = ‘Bu, D = NBu2)

We have designed and synthesised a new type of DTE-based platinum complex 2(o) (Chart 1) where the organometallic fragment, and the dialkylaminophenyl group are located on the same thiophene ring of the photochromic DTE unit (rather than at both ends of the DTE unit as in I(o)), the cyclometalated Pt(II) acetylide moiety being bounded to one of the reactive carbon atoms. This design gives rise to an extended π-conjugated alkynyl ligand in the open form, accompanied with metal-to-ligand/ligand-to-metal charge transfer (MLCT/LLCT) transitions. On the contrary, the formation of a tetrahedral centre at the C2 carbon in 2(e) induces a new conjugated pathway centered on the DTE. Moreover, the introduction of a strong donating dialkylamino

end group, allows to dramatically modify the electronic structure by protonation. Here, we present an unexpected sequential double modulation of the NLO properties of metal complexes.

Scheme 1 A three-state system: complex 2(o) and the prototated open-2H(o) and closed-ring isomers 2H+(c). i) HBF₄·OEt₂, CH₂Cl₂; ii) CH₂Cl₂, hv (350 nm); iii) CH₂Cl₂, hv (580 nm).

Complex 2 was synthesised by a standard procedure starting from (N=N=C)Pt-Cl and the appropriate DTE-based alkyne (Scheme S1, ESI†). The DTE-based ligand was prepared following a multi-step procedure. The two different thiophene derivatives were successively connected to the perfluorocyclopentene.

Fig. 1 Absorption spectral changes in CH₂Cl₂ at 298 K of complex 2(o) (red line), upon addition of HBF₄·OEt₂ (black line), after irradiation at 350 nm (blue line) and after irradiation at 580 nm (dashed black line).

The UV–vis absorption spectrum (CH₂Cl₂) of 2(o) is shown in Fig. 1 whereas the spectroscopic data are summarized in Tables S1 and S1 (ESI†). Complex 2(o) exhibits characteristic absorption bands for cyclometalated platinium(II) complexes, i.e., intraligand (IL) π–π* transitions of the DTE-based alkynyl and cyclometalated N=N=C ligands in the region of 300–370 nm and MLCT dx²–Pt → π*(N=N=C) mixed with some LLCT π(C=C–) → π*(N=N=C) transitions in the visible region. The spectrum of 2(o) extends up to 600 nm, as a result of the presence of an extended π-conjugated alkynyl ligand.
To further rationalize the absorption spectra, Time-Dependent DFT (TD-DFT) calculations have been carried out (see ESI† for computational details), using the PBE0\(^{15}\) hybrid functional and the Polarizable Continuum Model\(^{14}\) (PCM) to account for solvent effects. The computed transition wavelengths are listed in Table 1 whereas Fig. 2 gives the Natural Transition Orbitals\(^{15}\) (NTO) describing the \(S_0\rightarrow S_1\) transition for the different species. The \(S_0\rightarrow S_1\) transition in \(2(o)\) (computed at 573 nm) involves predominantly interligand charge transfer (LLCT) from the amino-DTE-acetylide ligand to the N\(\text{N}^\text{C}\) part coordinated to the Pt, with some metal-to-ligand (MLCT) charge transfer character. Moreover, theory predicts that the high-energy part of the spectrum of \(2(o)\) is dominated by transitions located on the ligands around the Pt atom (intraligand, IL) in agreement with expectations (see ESI†).

### Table 1. Experimental and computed absorption wavelengths (CH\(_2\)Cl\(_2\)). Theoretical calculations at the PCM-PBE0 level. The data between parenthesis are the oscillator strengths.

<table>
<thead>
<tr>
<th>(\lambda^{\text{Exp}}) [nm]</th>
<th>(\lambda^{\text{Theo}}) [nm] (f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(o)</td>
<td>362, 423, 483 (0.17), 372 (1.06), 465 (0.13), 573 (0.29)</td>
</tr>
<tr>
<td>2H(^+(o))</td>
<td>332, 440 (0.36), 369 (0.23), 410 (0.21), 485 (0.38)</td>
</tr>
<tr>
<td>2H(^+(c))</td>
<td>343, 380, 585 (0.23), 358 (0.14), 452 (0.10), 613 (0.30)</td>
</tr>
</tbody>
</table>

Interestingly, complex \(2(o)\) did not show any photoreactivity by irradiation with light at 350 nm in CH\(_2\)Cl\(_2\) or cyclohexane solution. It was previously advocated that a possible resonant cumulenic-quinoid form \(2(o)\) (see Scheme S3 in ESI) would be responsible of the inhibition of the photocyclization reaction,\(^{10}\) but DFT calculations based on Natural Bond Orbital\(^{16}\) (NBO) atomic charges and on inspection of the bond lengths in the optimized geometry indicate that \(2(o)\) has no significant contribution from this quinoid structure (see ESI†). The photochromic reactivity of the DTE moiety could be restored by protonation. Quaternization of the nitrogen atom of the dibutylamino end group was achieved by \(\text{in situ}\) addition of tetrafluoroboric acid (HBF\(_4\)\(\text{OEt}_2\)) into a CH\(_2\)Cl\(_2\) solution of \(2(o)\) (Scheme 1). The absorption spectrum of the protonated complex 2H\(^+(o)\) is blue-shifted over the whole electronic spectrum in comparison with \(2(o)\) (Fig. 1), as the result of the suppression of the strong electron-donating character of the dibutylamino end group.\(^{17}\) This analysis is supported by TD-DFT: the \(S_0\rightarrow S_1\) transition (computed at 485 nm) now involves CT from the DTE-acetylide moiety to the N\(\text{N}^\text{C}\) part with practical no participation of the amino group (Fig. 2). TD-DFT qualitatively preserves the electronic transition of \(2(o)\) that also has a large value of \(\mu\beta_{\text{EFISH}}\) (690 x 10\(^{-48}\) esu) but with inversion of the sign of the quadratic hyperpolarizability. Further irradiation at 350 nm (5 min) leads to ring closure, and to a high value of \(\mu\beta_{\text{EFISH}}\) (-925 x 10\(^{-48}\) esu) with again, a negative quadratic hyperpolarizability (see Table 2).

The second-order NLO response of \(2(o)\), 2H\(^+(o)\) and 2H\(^+(c)\) were determined by the EFISH method working in CH\(_2\)Cl\(_2\) at a concentration of 10\(^{-3}\) M with a non-resonant incident wavelength of 1.907 \(\mu\)m (see ESI†). Although it was traditionally used to study neutral molecules, the EFISH technique can be applied for the determination of the second-order NLO response of the systems having a negative value of \(\mu\beta\) with \(\mu\beta\) values of the same order of magnitude in agreement with the experimental findings (Table 2). Moreover, the NLO switching ability is confirmed by quantum chemistry calculations with both \(2(o)\) and 2H\(^+(c)\) systems having a negative quadratic hyperpolarizability contrarily to 2H\(^+(o)\) (Table 2).

![Fig. 2 NTO pairs corresponding to the \(S_0\rightarrow S_1\) electronic transition of systems \(2(o)\), 2H\(^+(o)\) and 2H\(^+(c)\) calculated with PBE0 functional (0.03 isovalue used).](image-url)
In conclusion, the novel DTE-based platinum(II) system is that the sign of the then upon irradiation with UV light. One key point in the system is that the sign of the $\mu$ response changes at each step.

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† Electronic supplementary information (ESI) available: Synthetic procedures, spectral characterization, EFISH measurements and computational details.

Notes and references


11 A similar design was reported by some of us for DTE-based hypridines, see: (a) V. Aubert, E. Eshow, F. Ibersiene, A. Boucekine, J. A. G. Williams, L. Toupet, R. Metivier, K. Nakatani, V. Guerchais and H. Le Bozec, New J. Chem., 2009, 33, 1320; (b) L. Ordonneau, J. Boixel, V. Aubert, M. S. Vidal, S. Moya, P. Aguirre, L. Toupet, J. A. G. Williams, H. Le Bozec and V. Guerchais, Org. Biomol. Chem., 2014, 12, 979.


Graphical Abstract