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Mixed-ligand Pt(II) dithione-dithiolato complexes: influence of the dicyanobenzodithiolato ligand on the second-order NLO properties†

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The mixed-ligand dithiolene complex $[Pt(Bz_2pipdt)(dcbdt)]$ (1) bearing the two ligands $Bz_2pipdt = 1.4$ dibenzyl-piperazine-3,2-dithione and dcbdt = dicyanobenzodithiolato, has been synthesized, characterized and studied to evaluate its second-order optical nonlinearity. The dithione/dithiolato character of the two ligands gives rise to an asymmetric distribution of the charge in the molecule. This is reflected by structural data showing that in the $C_2S_2PtS_2C_2$ dithiolene core the four sulfur atoms define a square-planar coordination environment of the metal where the Pt-S bond distances involving the two ligands are similar, while the C–S bond distances in the C_2S_2 units exhibit a significant difference in Bz_2 pipdt (dithione) and dcbdt (dithiolato). 1 shows a moderately strong absorption peak in the visible region, which can be related to a HOMO-LUMO transition, where the dcbdt ligand (dithiolato) contributes mostly to the HOMO, and the Bz₂pipdt one (dithione) mostly to the LUMO. Thus this transition has ligand-to-ligand charge transfer (CT) character with some contribution of the metal and undergoes negative solvatochromism and molecular quadratic optical nonlinearity ($\mu\beta_0 = -1296 \times 10^{-48}$ esu), which was determined by the EFISH (electric-field-induced second-harmonic generation) technique and compared with the values of similar complexes on varying the dithiolato ligand (mnt = maleonitriledithiolato, dmit = 2-thioxo-1,3-dithiole-4,5-dithiolato). Theoretical calculations help to elucidate the role of the dithiolato ligands in affecting the molecular quadratic optical nonlinearity of these complexes.

Introduction

Optical properties, in particular nonlinear (NLO) properties are of interest for a number of photonic applications, including high speed optical switching, telecommunications, optical data processing and storage.¹ Most often molecules with extensive

 π -delocalized system are required to promote NLO properties. Among these square-planar d⁸ metal-dithiolene asymmetric complexes at the molecular level, such as mixed-ligand complexes with dithione-dithiolato ligands, and a non-centrosymmetric crystal packing for a bulk material, are suitable to generate second-order NLO properties.² The potential of this class of complexes in generating second order NLO activity is currently under study by our group, through a systematic investigation on varying the metal, the *dithione* and the *dithiolato* ligand in order to reach a structure/property relationship useful to prepare complexes with optimized properties.³ A combined theoretical and experimental study on the triad $[M(II)(Bz_2pipdt)]$ (mnt)] (M(II) = Ni, Pd and Pt; Bz₂pipdt = 1,4-dibenzyl-piperazine-3,2-dithione; mnt = maleonitriledithiolato) has recently pointed out the main factors which affect the second order NLO activity.^{3b} It was found that the most appealing candidate in the metal triad was the platinum compound. This is related to: i) the most extensive mixture of the dithione/metal/dithiolato orbitals in the frontier orbitals (FOs); ii) the influence of the electric field of the solvent on the FOs that maximizes the difference in dipole moments between excited and ground state; and iii) the platinum compound having the largest oscillator strength. Accordingly we have selected platinum complexes to investigate the variation of the optical properties with the dithiolato ligand, while keeping

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[†] Electronic supplementary information (ESI) available: List of bond distances [Å] and angles [°] and DFT optimized geometries (Tables S1, S2); drawing, relative energy and percent compositions of the most significant orbitals obtained by DFT calculations in vacuum and in DMF (Tables S2, S3, S4, S5); Simulated visible spectra for [Pt(Bz₂pipdt) (dcbdt)] and [Pt(Bz₂pipdt)(dmit)] (Figures S1 and S2). CCDC reference number 848108. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt11956k

the dithione constant (Bz₂pipdt). Full characterization, including optical properties, for [Pt(Bz₂pipdt)(dmit)] (dmit = 2-thioxo-1,3dithiole-4,5-dithiolato) and [Pt(Bz2pipdt)(mnt)] is available, and in this work we report the study of [Pt(Bz₂pipdt)(dcbdt)] where dcbdt, dicvanobenzodithiolato, is a benzenoid-dithiolene where the electron withdrawing properties of the benzodithiolato ligand are improved by the presence of the cyano-substituents at the 4 and 5 positions of the aromatic ring. Among the square-planar metal d⁸ dithiolene complexes, benzodithiolates have been extensively investigated for their interesting electronic properties.⁴ In particular the assignment of the *innocent* or *noninnocent* character of these ligands has been an object of debate. The Jørgensen former definition, "ligands are innocent when they allow oxidation states of the central atoms to be defined",⁵ has been pointed out later on by Ward and McCleverty.⁶ Through the discussion of several examples, it was cleared up that the term noninnocent is applied properly when it refers to a particular combination of the metal and the ligand, where a significant mixing between the metal-centered and ligand-centered orbitals occurs, rather than to redox-active ligands alone. By taking into account the series $[Ni(LBu)_2]^{0, 1-, 2-}$ (LBu = 3,5-di-ter-buthylbenzene-1,2-dithiolato) and in particular structural results, it was proposed that the ligand behaves as a normal dithiolato (2-) implying the presence of the metal as formal Ni(II), Ni(III) and Ni(IV) for the members of the series⁷ in contrast to the enedithiolato-complexes case.⁸ Later on, theoretical and experimental studies from the Wieghardt group have shown that benzene-1,2dithiolato ligands may also behave as noninnocent ligands in their complexes.⁹

The synthesis and characterization of **1** allows us to compare the influence of the dithiolato ligand on the second-order NLO properties of dithione-dithiolato platinum(II) complexes, with the dithione being constant. In particular the selected ligands belong to a different class of dithiolato: dcbdt belongs to the class of benzodithiolato ligands; mnt to enedithiolato ones and dmit to dithiolato bearing a heterocycle (which contains in this case additional sulfur atoms) fused to the C_2S_2 moiety (see Chart 1 below). These complexes are useful to deepen the knowledge of the nature of bonding and to elucidate the factors which affect second-order NLO properties with a view to finding guidelines for designing candidates with controlled properties.

Experimental Section

General Comments

Reagents and solvents of reagent grade and spectroscopic grade (DMF, CH_3CN and CS_2) have been used as received from Aldrich. Microanalyses were performed by means of a Carlo Erba CHNS Elemental Analyzer model EA1108.

I.R. spectra (4000–350 cm^{-1}) were recorded on a Bruker IFS55 FT-IR Spectrometer as KBr pellets. Electronic spectra



were recorded with a Cary 5 spectrophotometer. Cyclic voltammograms were carried out on an EG&G (Princeton Applied Research) potentiostat–galvanostat model 273, by using a conventional three-electrode cell consisting of a platinum wire working electrode, a platinum wire as counter-electrode and Ag/AgCl in saturated KCl solution as reference electrode. The experiments were performed at room temperature (25 °C), in dry and argon-degassed DMF containing 0.1 mol dm⁻³ Bu₄NBF₄ as supporting electrolyte, at 25–200 mV s⁻¹ scan rate.

 $[Pt(Bz_2pipdt)(dcbdt)]$ (1). $(Bu_4N)_2[Pt(dcbdt)_2]$ (25.74 mg) in 25 cm³ of CH₃CN (green solution) was added drop-wise to a dark red suspension of [Pt(Bz₂pipdt)Cl₂] (16,50 mg) in 25 cm³ CH₃CN, under stirring and reflux (see Results and Discussion section, where related references are quoted). After one day a dark-blue solid was formed (17.82 mg; yield: 89%). This solid was filtered, washed with diethyl ether and then dried. Well formed crystals suitable for X-ray crystallography were obtained through re-crystallization from DMF/diisopropyl ether. Analytical results are in accordance with the formula [Pt(Bz₂pipdt) (dcbdt)]. Anal. Found: C, 43.7; H, 2.9; N, 7.5, S, 17.7. Calc. for C₂₆H₂₀N₄PtS₄: C, 43.9; H, 2.8; N, 7.9; S, 18.0. IR (KBr pellets) 2964 vw, 2854 vw, 2221vs, 1611vw, 1531vs, 1506 m 1453w, 1434w, 1404w, 1386 m, 1363vs, 1308 m, 1246w, 1218vs, 1114 m, 1051w, 1030w, 892w, 733w, 695w, 683vw, 622vw, 618vw, 548vw, 527w, 498vw, 448vw, 422vw.

EFISH experiments were performed using a freshly prepared 10^{-3} M solution in DMF and working with a 1907 nm incident wavelength, obtained by Raman shifting the 1064 nm emission of a Q-switched Nd:YAG laser in a high pressure hydrogen cell (60 bar). A liquid cell with thick windows in the wedge configuration was used to obtain the Maker fringe pattern (harmonic intensity variation as a function of liquid cell translation). In the EFISH experiments the incident beam was synchronized with a DC field applied to the solution, with 60 and 20 ns pulse duration, respectively, in order to break its centro-symmetry. From the concentration dependence of the harmonic signal with respect to that of the pure solvent, the NLO responses were determined (assumed to be real because the imaginary part has been neglected) from the experimental value γ_{EFISH} , through eqn (1):

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

where γ_{EFISH} is the sum of a cubic electronic contribution $\gamma(-2\omega; \omega, \omega, 0)$ and of a quadratic orientational contribution $\mu\beta_{\lambda}$ $(-2\omega; \omega, \omega)/5kT$, with μ being the ground state dipole moment, and β_{λ} the projection along the dipole moment direction of the vectorial component β_{vec} of the tensorial quadratic hyperpolarizability working with the incident wavelength λ . Twelve successive measurements have been performed and the obtained values averaged.

X-ray Crystallography

A summary of data collection and structure refinement for [Pt (Bz₂pipdt)(dcbdt)] is reported in Table 1. Single crystal data were collected with a Bruker Smart APEXII area detector diffractometer, Mo-K α : $\lambda = 0.71073$ Å. The unit cell parameters were obtained using 60 ω -frames of 0.5° width and scanned from three different zones of the reciprocal lattice. The intensity

Table 1	Summary	of	X-ray	crystallographic	data	for	Pt(Bz ₂ pipdt)
(dcbdt)]							

	[Pt(Bz ₂ pipdt)(dcbdt)]
Empirical formula	C26H20N4PtS4
Formula weight	711.79
Color, habit	Black, prism
Crystal size/mm	$0.25 \times 0.10 \times 0.07$
Crystal system	Orthorhombic
Space group	Pbcn
a/Å	21.151(2)
b/Å	16.300(1)
$c/\text{\AA}$	7.921(1)
α (°).	90
β (°).	90
γ (°).	90
$V/Å^3$	2730.9(5)
Ζ	4
<i>T</i> /K	293(2)
ρ (calc). Mg m ⁻³	1.731
μ/mm^{-1}	5.466
θ range/°	1.58 to 28.63
No. of reflections/unique	36999/3513
GooF	1.004
<i>R</i> 1	0.0286
wR2	0.0561
${}^{a}R1 = \Sigma Fo - Fc / \Sigma Fo , wR2 = [\Sigma[w] 1/[\sigma2(Fo2) + (aP)2 + bP], where P = [m]$	$(Fo2-Fc2)2]/\Sigma[w(Fo2)2]]_{\frac{1}{2}}, w = \max(Fo2,0) + 2Fc2]/3$

data were integrated from several series of exposures frames $(0.3^{\circ} \text{ width})$ covering the sphere of reciprocal space.¹⁰ An absorption correction was applied using the program SADABS¹¹ with min. and max. transmission factors of 0.652 and 1.000, respectively. The structure was solved by direct methods (SIR2004)¹² and refined on F^2 with full-matrix least squares,¹³ using the Wingx software package.¹⁴ Non hydrogen atoms were refined anisotropically and the hydrogen atoms were placed at their calculated positions. Graphical material was prepared with the Mercury 2.0¹⁵ and ORTEP3 for Windows¹⁶ programs. CCDC 848108 contains the supplementary crystallographic data for this paper.[†]

Computational details

The electronic properties of the $[Pt(Bz_2pipdt)(dcbdt)]$ and $[Pt(Bz_2pipdt)(dmit)]$ complexes were investigated by means of DFT methods.¹⁷ The molecular structures of the complexes were optimized starting from the experimental geometries derived by the X-ray structural characterization using no symmetry constraints. The Becke three-parameter exchange functional with Lee–Yang–Parr correlation functional $(B3LYP)^{18,19}$ was employed together with the 6-311G(d,p) basis set^{20,21} for the C, H, N, and S atoms. The Pt atom was treated with SDD valence basis set,^{22–24} and with the MWB60 effective core potentials in order to take into account relativistic effects.

To address DMF solvation effects, the conductor-like screening model as developed in the polarisable continuum model (CPCM),²⁵ has been applied with united atom topological model atomic radii (DMF parameters: $\varepsilon = 37.21$, molar volume = 77.41, density = 0.0079, solvent radius = 2.647 Å).²⁶ Single point CPCM calculations of the complexes were performed using gas-phase optimized geometries. TD-DFT^{27,28} was used to calculate the energies of the five lowest singlet electronic transitions. The dipole moment difference between the excited and ground states ($\Delta \mu_{ge}$) was calculated by using the finite field approach (external field strength of ±0.0005 atomic units).²⁹ All the calculations were performed with the Gaussian 03 program.³⁰ AOMix was used for determining atomic orbital compositions employing Mulliken Population Analysis,³¹ and SWizard³² was used to analyze the electronic transitions obtained from TD-DFT calculations.

Results and Discussion

As shown in Scheme 1:



[Pt(Bz₂pipdt)(dcbdt)], has been obtained by reacting [Pt (Bz₂pipdt)Cl₂] with (Bu₄N)₂[Pt(dcbdt)₂],³³ following a procedure which has shown to work well for the preparation of the corresponding [Pt(Bz₂pipdt)(dmit)] complex.^{3a} In these cases, the desired dianion, which is less stable when uncoordinated, is provided by salts of platinum (or also nickel) dianionic complexes, and Bu₄NCl and degradation products containing the metal cations are formed. The use of alkaline salts of dithiolato as direct anion source is preferable, when they have been previously isolated and their stability allows it (for example in the Na₂mnt case).^{3b} The starting reagent [Pt(Bz₂pipdt)Cl₂] was prepared by mixing, in CH₃CN under reflux, equimolar amount of Bz₂pipdt and [Pt(DMSO)₂Cl₂].³⁴ On slow evaporation of the solvents, well formed dark-blue crystals precipitated in high yield (~90%). These crystals were suitable for X-ray diffractometric characterization, which shows that 1 crystallizes in the orthorhombic Pbcn space group. A summary of the X-ray crystallographic data and selected bond lengths and angles for 1 are reported in Tables 1 and 2. The molecular drawing of 1 is depicted in Fig. 1, which shows that four sulfur atoms from the two different ligands define the coordination environment of the metal, which is in a slightly distorted square-planar geometry.

As reported in Table 2, the Pt–S bond distances involving the dcbdt ligand are only slightly shorter than those originating from Bz₂pipdt.

At variance, the C–S bond distances of dcbdt are significantly longer than those of Bz₂pipdt (1.751(4) vs. 1.688(4) in Å), which is in accordance with the different natures of the ligands with prevailing dithiolato character for dcbdt and dithione one for Bz₂pipdt.

In Fig. 2 the crystal packing of 1, projected along the *c* axis is shown. The Pt atoms are located between two hexa-atomic rings of the Bz₂pipdt ligand, and the distance between the centroid of the ligand and the Pt atom is of approximately 4 Å.

Most significant vibrations (IR spectra) are found at approximately 1531 cm⁻¹, (the typical C–N vibrations of thioamidic groups) while dcbdt exhibits peaks due to v(CN) at 2221 cm⁻¹.

Table 2	Selected	Experimental	and	calculated	(see	related	section)
bond dista	ances (Å)	and angles (°)	for [I	Pt(Bz2pipdt))(dcbo	:tt)]	

	Exp.	Calc.
Pt–S (dcbdt)	2.273(1)	2.314
Pt-S (Bz ₂ pipdt)	2.278(1)	2.314 2.339
S–C (dcbdt)	1.751(4)	2.339 1.753
S-C (Bz ₂ pipdt)	1.688(4)	1.753 1.702
C–C (dcbdt)	1.390(7)	1.702 1.411
C–C (Bz ₂ pipdt) C–N (Bz ₂ pipdt)	1.484(8) 1.323(4)	1.460 1.363
S–M–S (dcbdt)	89.88(5)	1.363 88.95
S-M-S (Bz ₂ pipdt) M-S-C (dcbdt)	88.27(5) 103.7(1)	86.52 104.05
M–S–C (Bz ₂ pipdt)	105.8(1)	104.05 105.84
S-C-C (dcbdt)	121.3(1)	105.84 121.48
S-C-C (Bz ₂ pipdt)	119.9(1)	121.48 120.78
		120.78



Fig. 1 Ortep drawing of $[Pt(Bz_2pipdt)(dcbdt)]$ (1) with thermal ellipsoids drawn at the 30% probability level. Symmetry code ' = -x; y; $\frac{1}{2}$ - z.



Fig. 2 Crystal packing of $[[Pt(Bz_2pipdt)(dcbdt)]$ projected along the *c* axis. The Pt atoms are located between two hexa-atomic rings of the Bz_2pipdt ligand.



Fig. 3 Solvatochromic behaviour of 1 in DMF/CS₂ mixtures ranging from DMF 100% to 20%. The energy of the solvatochromic peak of 1 *versus* the solvent polarity parameter for solutions from DMF 100% to 20% follows a straight line with slope 1.2.

CC stretching vibrations, which are a convenient marker for the oxidation level of a given coordinated dithiolene ligand in the case of nonbenzenoid-dithiolenes,³⁵ do not work well in the case of benzenoid ligands. In fact in benzenoid dithiolene complexes the chelate ring C–C distance, differently to the ene-dithiolato cases, undergoes only small variation with the charge in the *o*-phenylene moiety, while C–S distances in the C₂S₂ units are more dependent on the charge of the ligand.³⁶

Complex 1 is characterized in the visible region by a broad absorption at 711 nm in DMF with medium molar absorption coefficient [$10.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$] and a negative solvatochromism, as shown in Fig. 3. The energy of the solvatochromic peak shows a linear dependence on the solvent polarity parameter proposed by Cummings and Eisenberg for d⁸-metal diimine-dithiolato complexes.³⁷ The solvatochromic shift determined as the gradient of this plot falls in the range found for d⁸-metal diimine-dithiolato complexes which exhibit relatively high values of molecular hyperpolarizability.^{2c}

This solvatochromic peak has been assigned for both these classes of complexes to a mixed-metal-ligand-to-ligand charge transfer (MMLL'CT) HOMO \rightarrow LUMO transition.^{36,37} EFISH (electric field induced second harmonic generation) experiments have been performed using a freshly prepared 10^{-3} M solution in DMF and working with a 1907 nm incident wavelength, obtained by Raman shifting the 1.064 nm emission of a Qswitched Nd:YAG laser in a high pressure hydrogen cell (60 bar), as described in detail in the Experimental Section. The set up used allows the determination of the scalar product $\mu\beta_{\lambda}(\mu =$ ground state dipole moment; β_{λ} = projection of the vectorial component of the quadratic hyperpolarizability tensor along the dipole moment axis). The $\mu\beta_{\lambda}$ values determined at 1907 nm incident wavelength have been extrapolated to zero frequency applying the equation: $\beta_0 = \beta_{\lambda} [1 - (2\lambda_{\max}/\lambda)^2] [1 - (\lambda_{\max}/\lambda)^2]$. These values are collected in Table 3.

Cyclic voltammetric experiments performed on DMF solutions of the complex exhibit two reversible reduction waves and one irreversible oxidation wave. CV data are collected in Table 4.

The reduction processes, see the CV scans in Fig. 4, show reduction values close to those found for other mixed-ligand complexes bearing R_2pipdt ligands. Instead the oxidation potential (E_a) falls between those of dmit and of mnt, suggesting a

Table 3 Optical and EFISH results for $[Pt(Bz_2pipdt)(L)]$ (L = dcbdt; mnt; dmit) complexes

Complex [Pt(Bz ₂ pipdt)(L)]	$\lambda_{\max}^{a/a}$ /nm	$\varepsilon (\times 10^{-3} \text{mol}^{-1} \text{dm}^3 \text{cm}^{-1})$	$\mu \beta^{a,b} / 10^{-48}$ esu $\mu \beta_0 / 10^{-48}$ esu	Ref.
L = mnt	685	10.1	-1950 -822	3b
L = dcbdt	711	10.6	-3390 -1296	This work
L = dmit	827	14.8	-10000 -2011	3a

 a in DMF; b the uncertainty of the measure is between \pm 3 and \pm 5.5%.

Table 4 Cyclic voltammetric Data. Measured at Pt electrode in DMF), $0.1 \text{ M Bu}_4\text{NPF}_6$, scan rate 100 mV s⁻¹ (Reference Electrode Ag/AgCl)

[Pt(Bz ₂ pipdt)(L)]	$\begin{array}{c} E_{\rm a}({\rm V})^a \ 0 \rightarrow \\ 1+ \end{array}$	$E^{1}_{1/2}(V)^{b} 0 \leftrightarrows$	$E^{2}_{1/2}(V)^{b} 1 - \Leftrightarrow$
$L = mnt^{3b}$	+1.09	-0.37	-0.87
L = dcbdt	+1.04	-0.38	-0.86
$L = dmit^{3a}$	+0.86	-0.39	-0.84

 a irreversible anodic broad wave; b reversible reduction waves (linear dependence of the peak currents (ip) from the square root of the voltage scan rate with $\rm ip_{red}/\rm ip_{ox}$ close to the unity).

similar sequence for the ease of the one electron removal process. Electrochemical results are consistent with spectroscopic findings and with theoretical results (see related discussion in the next section). It is found that the ligand acting as dithione gives a prevalent contribution to the LUMO (relatable to reduction processes) and the ligand acting as dithiolato to the HOMO (relatable to the oxidation process).

The very similar $E_{1/2}$ values for the reduction processes and the oxidation potential sequence are in accordance with the energetic sequence of the FOs. Moreover the redox activity, which is related to the frontier orbitals involved in the CT transition responsible of the solvatochromic peak, suggests these complexes may exhibit redox-switching of molecular first hyperpolarizabilities.³⁸ A suitable processing of the material (for example processing it into an electro-conducting thin-film)³⁹ is required for its possible application in optical devices.

Theoretical studies

The electronic properties of the $[Pt(Bz_2pipdt)(dcbdt)]$ complex as well as those of the $[Pt(Bz_2pipdt)(dmit)]$ were investigated by means of DFT methods and compared with those previously reported for $[Pt(Bz_2pipdt)(mnt)]$.^{3b} For comparison purposes the choice of the level of theory and method employed in this work was consistent with that adopted for $[Pt(Bz_2pipdt)(mnt)]$. The molecular structures of both complexes were optimized starting from the X-ray experimental geometries (Tables S1, S2 and S3 in the Supplementary Material†). In general there is good agreement between the DFT-optimized and experimental geometries, even though the coordination bond lengths are slightly overestimated by the calculations (~0.04 Å), Tables 2, S2 and S3.† For



Fig. 4 Cyclic voltammograms of **1** recorded at 293 K with different scan rates in a DMF solution containing 0.1 M TBABF₄.

both compounds, the most relevant difference between the experimental and optimized geometries is in the orientation of the peripheral benzyl groups of the Bz_2 pipdt ligands.

As usually found in square-planar metal d⁸-dithiolene complexes, the four sulfur atoms are forced into close proximity in the ligand cage as a consequence of the metal coordination and a significant intra- and inter-ligand repulsive interaction of the S…S type occurs.^{4a} As a result, ligand orbitals are significantly destabilized as compared to the metal's d-orbitals which are found at lower energies. This situation gives rise to the so called *inverted bonding scheme* (in a normal bonding scheme the metal d orbitals lie at higher energies compared to the ligand orbitals).^{4a–c}

The electronic structures of both complexes were evaluated both in a vacuum and by taking into account the contribution of the solvent (DMF) by means of the CPCM method. In Tables 5, 6, and S4–S7† the energies along with the contour plots of the frontier orbitals of [Pt(Bz₂pipdt)(dcbdt)] and [Pt(Bz₂pipdt) (dmit)] are reported, whereas those of the mnt derivative are available in ref. 3b. The HOMO and LUMO are both formed from the out-of-plane antibonding interactions between the metal's d_{xz} orbital and a ligand based C₂S₂ orbital (with C–C π and C–S π^* character). By inspecting the shape of the HOMO and LUMO, it is evident that the former is mainly located on the dithiolato ligand, whereas the latter is on the dithione one.

This picture is more clearly evidenced by analyzing the contribution of three molecular fragments (the two ligands and the metal) to the molecular orbitals, Fig. 5 and Tables 5 and 6. In fact at least 70% of the HOMO is due to the dithiolato ligand, whereas the dithione ligand mostly contributes to the LUMO. The contribution of different fragments (the two ligands and the central metal) to the complexes' frontier orbitals is consistent with π^* -back-donation theory.^{3b,40} It can also be appreciated how the presence of a relatively polar solvent such as DMF influences the composition of these frontier orbitals; in fact, in DMF, the HOMO and LUMO become even more localized on the dithiolato and dithione ligands, respectively. Furthermore, the presence of DMF also influences their energy levels since the HOMO–LUMO gap increases by 0.3 eV for both compounds as

	E(AV)	Fragment composition (%)			
Gas phase	E(ev)	Pt	Bz ₂ pipdt	debdt	
LUMO	-3.85	6.3	78.4	15.3	
номо	-5.47	8.4	23.3	68.3	
HOMO-LUMO gap DMF	1.62				
LUMO	-3.72	4.6	88.2	7.2	
номо	-5.64	13.7	17.6	68.7	
HOMO-LUMO gap	1.92				
		989 152 988 152 142 41 988 152 142 4.1 142 4.1 191 117 19.1	29 117 29 29		

Table 5 Spatial plots of HOMO and LUMO (isovalue = 0.04) of [Pt(Bz₂pipdt)(dcbdt)] in the gas phase and in DMF (B3LYP/6-311G(d,p)-SDD), together with the contribution of different fragments to these orbitals

Fig. 5 a) Percentage contributions of different atoms to frontiers molecular orbitals²² of $[Pt(Bz_2pipdt)(dcbdt)]$ (HOMO, below and LUMO, above) on the left side. b) Percentage contributions of different atoms to frontiers molecular orbitals²² of $[Pt(Bz_2pipdt)(dmit)]$ (HOMO, below and LUMO, above) on the right side. CPCM (DMF) B3LYP/6-311G(d,p)-SDD.

a consequence of the HOMO stabilization, and in the case of [Pt $(Bz_2pipdt)(dcbdt)$], also of the LUMO destabilization.

a)

The shapes of the frontier orbitals, and the data reported in Tables 5 and 6, suggest that the HOMO–LUMO transition will

have mixed metal–ligand to metal–ligand character (MMLL' CT). Related data on $[Pt(Bz_2pipdt)(mnt)]$ are available in ref. 3b. The HOMO–LUMO energy gap in $[Pt(Bz_2pipdt)(L)]$ follows the order: mnt > dcbdt > dmit either in vacuum or in the presence of

b)



Table 6 Spatial plots of HOMO and LUMO (isovalue = 0.04) of [Pt(Bz₂pipdt)(dmit)] in the gas phase and in DMF (B3LYP/6-311G(d,p)-SDD), together with the contribution of different fragments to these orbitals

the solvent and this can be explained by considering that the HOMO is an antibonding MO mainly localized on the dithiolato ligands.

The shape of the HOMO in the three complexes showing an increase of the antibonding character (M-S; C-Sthiol in mnt derivative; S-M; C-S_{thiol} and C11-C12 in dcbdt derivative; M-S, C-S_{endo} and C-S_{exo} in dmit derivative) on going along the series mnt, dcbdt, and dmit is in agreement with the increase of the corresponding HOMO energies. Vertical excitation energies of [Pt(Bz₂pipdt)(dcbdt)] and [Pt(Bz₂pipdt)(dmit)] were determined using time-dependent density functional theory (TD-DFT) as described in the Experimental section. These calculations were performed in three different conditions: 1) in the gas phase, 2) in the presence of chloroform as solvent, and 3) in the presence of DMF as solvent. A comparison between the energies of the transitions in chloroform and in DMF was performed in order to investigate the solvatochromic behavior of these complexes. The first five singlet-singlet excitation energies are reported in Tables 7 and 8. The first allowed transition is characterized by the greater oscillator strength and is mainly composed of a HOMO to LUMO excitation, supporting its assignment as MMLL' CT transition for both complexes. These results are in agreement with previous calculations performed for the [Pt(Bz₂pipdt)(mnt)] complex.^{3b} The negative solvatochromism of these complexes is also confirmed by comparing the calculated absorption spectra in DMF and chloroform, Figures **Table 7** Low-lying singlet excited states of $[Pt(Bz_2pipdt)(dcbdt)]$ computed by TD-DFT/CPCM(DMF) with the orbitals involved in the excitations, vertical excitation energies (ΔE), oscillator strength (f), and character of the CT transitions. The principal singlet transition responsible for the main absorption band in the visible region is shown in bold

State	Composition	$\Delta E (eV)/\lambda(nm)$	f	Character
1	HOMO → LUMO, 79%	1.68/739	0.3500	dcbdt/Pt/Bz ₂ pipdt \rightarrow Bz ₂ pipdt (MMLL_CT)
2	HOMO-1 → LUMO, 91%	1.80/689	0.0009	$\begin{array}{l} \text{(MMEL C1)} \\ \text{dcbdt/Pt/Bz_pipdt} \\ \rightarrow Bz_pipdt \\ (MMLL CT) \end{array}$
3	HOMO-2 → LUMO, 97%	2.26/549	0.0008	$Pt \rightarrow Bz_2pipdt$
4	HOMO-3→ LUMO, <i>94%</i>	2.73/454	0.0276	$\begin{array}{l} \text{(NLCT)}\\ \text{Bz_2pipdt} \rightarrow \\ \text{Bz_2pipdt}\\ \text{(ILCT)} \end{array}$

S1 and S2.† Basically, the calculated first singlet–singlet transition in DMF is in reasonable agreement with the experimental results. In fact, the absorption spectra of $[Pt(Bz_2pipdt)(dcbdt)]$ recorded in DMF exhibits a λ_{max} of 711 nm to be compared to the value of 738 nm derived by the TD-DFT calculations. A worse agreement is found for $[Pt(Bz_2pipdt)(dmit)]$ since the

State	Composition	$\Delta E (eV)/\lambda(nm)$	f	Character
1	HOMO → LUMO, 73%	1.30/951	0.3410	$\frac{\text{dmit/Pt/Bz_2pipdt}}{\text{Bz_2pipdt}}$
2	HOMO-1 → LUMO, 89%	1.87/662	0.0023	$\begin{array}{l} \text{(MNLL CT)} \\ \text{dmit/Pt/Bz_2pipdt} \rightarrow \\ \text{Bz_2pipdt} \\ \text{(MMLL CT)} \end{array}$
3	HOMO-4 → LUMO, 98%	2.24/555	0.0005	$Pt \rightarrow Bz_2pipdt$
4	HOMO→ LUMO+2, <i>93%</i>	2.31/537	0.0023	(MLCT) dmit/Pt/Bz₂pipdt → dmit/Pt/Bz₂pipdt (MMLL CT)

experimental λ_{max} in DMF is 827 nm, whereas the calculations yield a value of 951 nm. Nevertheless the trend observed for the three complexes [Pt(Bz₂pipdt)(mnt)], [Pt(Bz₂pipdt)(dcbdt)] and [Pt(Bz₂pipdt)(dmit)] agrees well with the experimental results. In fact the electron withdrawing properties of the dithiolato ligands and the amount of mixing of their π orbitals in the HOMO are in agreement with the observed electrochemical and optical trends (oxidation process and λ_{max} at decreasing potentials and decreasing energy respectively for mnt > dcbdt > dmit derivatives).

The combined experimental and theoretical results help to elucidate the factors affecting NLO properties. By taking into account a simplified two-state model⁴¹ the second-order polarizability, is given by:

$$\beta \propto \frac{3\Delta\mu_{\rm ge}(\mu_{\rm ge})^2}{\left(E_{\rm max}\right)^2} \tag{2}$$

The $\Delta \mu_{ge}$ for the three complexes is around -8 Debye, hence it is not expected to influence the value of β along the series. On the other hand, the μ_{ge} varies in the following order $\mu_{ge}(\text{dmit}) \approx \mu_{ge}(\text{dcbdt}) > \mu_{ge}(\text{mnt})$, while the energy of the transition E_{ge} is in the order $E_{ge}(\text{mnt}) > E_{ge}(\text{dcbdt}) > E_{ge}(\text{dmit})$. Thus the lower energy gap in [Pt(Bz_2pipdt)(dmit)], due to the higher antibonding nature of the HOMO, seems to be responsible for the higher second-order polarizability among the complexes investigated here.

Conclusions and Outlook

The redox-active mixed-ligand dithiolene complex [Pt(Bz₂pipdt) (dcbdt)] bearing the two ligands $Bz_2pipdt = 1,4$ -dibenzyl-piperazine-3,2-dithione and dcbdt = dicyanobenzodithiolato, has been synthesized, characterized and studied by the EFISH method to evaluate its second-order optical nonlinearity. The properties of 1 were compared with those of the corresponding [Pt(Bz₂pipdt) (L)] L = mnt, dmit complexes. DFT and TD-DFT calculations helped to elucidate the electronic structure of these complexes indicating the role of the dithiolato ligands. Furthermore, the employment of the CPCM model reveals the role of the solvent in defining the electronic properties of the complexes. In particular, the presence of a polar solvent stabilizes the HOMO, which is mainly localized on the dithiolato ligand, whereas it destabilizes the LUMO, which is mainly localized on the dithione one. These results are in agreement with experimental electronic spectra and electrochemical data for the complexes under study. All these complexes show large negative second-order polarizability values, amongst the highest reported so far for metal complexes. The factors affecting these high negative second-order polarizability values are related to the high difference in dipole moments between excited and ground state enhanced by the electric field of the solvent, the large oscillator strength for the charge transfer transition, and the relatively low energy gap. In particular, in [Pt(Bz₂pipdt)(dmit)] the more extensive antibonding nature of the HOMO induces a smaller energy gap providing a larger β_0 value. The redox activity of these complexes, which is related to the frontier orbitals involved in the CT transition responsible of the solvatochromic peak, suggests these complexes deserve to be investigated further for possible redoxswitching of molecular first hyperpolarizability.38

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References

- (a) N. J. Long, Angew. Chem., Int. Ed. Engl., 1995, 34, 21;
 (b) D. M. Roundhill and J. P. Fackler, Optoelectronic Properties of Inorganic Compound, Plenum Press, New York, 1999;
 (c) E. Cariati, M. Pizzotti, D. Roberto, F. Tessore and R. Ugo, Coord. Chem. Rev., 2006, 250, 1210–1233;
 (d) S. Di Bella, C. Dragonetti, M. Pizzotti, D. Roberto, F. Tessore and R. Ugo, in Molecular Organometallic Materials for Optics Topics in Organometallic Chemistry, ed. H. Le Bozec and V. Guerchais, 2010, 28, 1–55.
- 2 (a) B. J. Coe, in *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, vol. 9, Elsevier-Pergamon, Oxford, 2004, 621–687; (b) P. Deplano, M. L. Mercuri, A. Serpe and L. Pilia, in *Structure and Properties of d⁸-Metal Dithiolene Complexes Chapter 16 in The chemistry of metal enolates*, ed. J. Zabicky, Wiley& Sons, Ltd, 2009, 879–928.
- 3 (a) D. Espa, L. Pilia, L. Marchiò, M. L. Mercuri, A. Serpe, A. Barsella, A. Fort, S. J. Dalgleish, N. Robertson and P. Deplano, *Inorg. Chem.*, 2011, **50** (6), 2058–2060; (b) L. Pilia, D. Espa, A. Barsella, A. Fort, C. Makedonas, L. Marchiò, M. L. Mercuri, A. Serpe, C. A. Mitsopoulou and P. Deplano, *Inorg. Chem.*, 2011, **50**, 10015–10027.
- 4 (a) R. K. Szilagyi, B. S. Lim, T. Glaser, R. H. Holm, B. Hedman, K. O. Hodgson and E. I. Solomon, *J. Am. Chem. Soc.*, 2003, **125**, 9158–9169; (b) S. Sproules and K. Wieghardt, *Coord. Chem. Rev.*, 2011, **255**, 837–860; (c) G. Bruno, M. Almeida, F. Artizzu, J. C. Dias, M. L. Mercuri, L. Pilia, C. Rovira, X. Ribas, A. Serpe and P. Deplano, *Dalton Trans.*, 2010, **39**, 4566.
- 5 K. Jørgensen, Coord. Chem. Rev., 1966, 1, 164.
- 6 M. D. Ward and J. A. McCleverty, J. Chem. Soc., Dalton Trans., 2002, 275–288.
- 7 D. Sellmann, H. Binder, D. Häusinger, F. W. Heinemann and J. Sutter, Inorg. Chim. Acta, 2000, 300 (02), 829.
- 8 B. S. Lim, D. V. Fomitchev and R. H. Holm, *Inorg. Chem.*, 2001, 40, 4257.

- 9 (a) K. Ray, T. Weyhermüller, F. Neese and K. Wieghardt, *Inorg. Chem.*, 2005, 44, 5345; (b) T. Petrenko, K. Ray, K. Wieghardt and F. Neese, *J. Am. Chem. Soc.*, 2006, 128, 4422.
- 10 SMART (control) and SAINT (integration) software for CCD systems, Bruker AXS, Madison, WI, USA, 1994, 2008.
- 11 Area-Detector Absorption Correction; Siemens Industrial Automation, Inc.: Madison, WI, 1996.
- 12 M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori and R. Spagna, SIR2004: an improved tool for crystal structure determination and refinement 35, *J. Appl. Crystallogr.*, 2005, **38**, 381–388.
- 13 G. M. Sheldrick, SHELX97. Programs for Crystal Structure Analysis 1997 (Release 97-2), University of Göttingen, Germany. 2008.
- 14 L. J. Farrugia, WinGX suite for small-molecule single-crystal crystallography, J. Appl. Crystallogr., 1999, 32 (4), 837–838.
- 15 C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, 39, 453–457.
- 16 L. J. Farrugia, ORTEP-3 for Windows a version of ORTEP-III with a Graphical User Interface (GUI), J. Appl. Cryst., 1997, 30 (1), 568.
- 17 R. G. Parr and W. Yang, Density-Functional Theory of Atoms and Molecules; Oxford University Press: New York, 1989, 2010.
- 18 A. D. Becke, Phys. Rev. A: At., Mol., Opt. Phys., 1988, 38 (6), 3098– 3100.
- 19 A. D. Becke, J. Chem. Phys., 1993, 98 (7), 5648-5652.
- 20 R. Ditchfield, W. J. Hehre and J. A. Pople, J. Chem. Phys., 1971, 54, 724.
- 21 V. A. Rassolov, M. A. Ratner, J. A. Pople, P. C. Redfern and L. A. Curtiss, J. Comput. Chem., 2011, 22, 976.
- 22 P. Fuentealba, H. Preuss, H. Stoll and L. V. Szentpaly, *Chem. Phys. Lett.*, 1989, **89**, 418.
- 23 X. Y. Cao and M. Dolg, THEOCHEM, 2002, 581, 139.
- 24 P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker and P. D. W. Boyd, *J. Chem. Phys.*, 1989, **91**, 1762.
- 25 M. Cossi, N. Rega and G. Scalmani, V. Barone, *J. Comput. Chem.*, 2003, 24 (6), 669–681.
- 26 V. Barone, M. Cossi and J. Tomasi, J. Chem. Phys., 1997, 107 (8), 3210– 3221.
- 27 M. E. Casida, C. Jamorski, K. C. Casida and D. R. Salahub, J. Chem. Phys., 1998, 108 (11), 4439–4449.
- 28 R. E. Stratmann, G. E. Scuseria and M. J. Frisch, J. Chem. Phys., 1998, 109 (19), 8218–8224.
- 29 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin,

- J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision C.02)*, Gaussian, Inc., Wallingford, CT, 2004.
- 30 GaussView, Version 3.09, R. Dennington II, T. Keith, J. Millam, K. Eppinnett, W. L. Hovell, R. Gilliland, Semichem, Inc., Shawnee Mission, KS, 2003, 2010.
- 31 S. I. Gorelsky, AOMix: Program for Molecular Orbital AnalysisUniversity of Ottawa, 2011, http://www.sg-chem.net/.2011
- 32 S. I. Gorelsky, SWizard program, revision 4.6, http://www.sg-chem.net/ .2011
- 33 H. Alves, D. Simão, I. C. Santos, V. Gama, R. T. Henriques, H. Novais and M. Almeida, *Eur. J. Inorg. Chem.*, 2004, 1318–1329.
- 34 Y. N. Kukushkin, Y. E. Viez'menskii and L. I. Zorina, Russ. J. Inorg. Chem., 1968, 835.
- 35 (a) K. I. Pokhodnya, C. Faulmann, I. Malfant, R. Andreu-Solano, P. Cassoux, A. Mlayah, D. Smirnov and J. Leotin, *Synth. Met.*, 1999, 103, 2016; (b) H. H. Wang, S. B. Fox, E. B. Yagubskii, L. A. Kushch, A. I. Kotov and M.-H. Whangbo, *J. Am. Chem. Soc.*, 1997, 119, 7601.
- 36 P. Deplano, L. Pilia, D. Espa, M. L. Mercuri and A. Serpe, *Coord. Chem. Rev.*, 2010, 254, 1434–1447.
- 37 (a) S. D. Cummings and R. Eisenberg, J. Am. Chem. Soc., 1996, 118, 1949–1960; (b) S. D. Cummings, L-T. Cheng and R. Eisenberg, Chem. Mater., 1997, 9, 440.
- 38 B. J. Coe, Acc. Chem. Res., 2006, 39, 383-393.
- 39 S. Dalgleish and N. Robertson, Chem. Commun., 2009, 5826.
- 40 (a) C. Makedonas and C. A. Mitsopoulou, *Inorg. Chim. Acta*, 2007, 360, 3997; (b) C. Makedonas and C. A. Mitsopoulou, *Eur. J. Inorg. Chem.*, 2007, 4176; (c) C. Makedonas, C. A. Mitsopoulou, F. J. Lahoz and A. I. Balana, *Inorg. Chem.*, 2003, 42, 8853.
- 41 (a) J. L. Oudar and D. S. Chemla, J. Chem. Phys., 1977, 66, 2664;
 (b) S. Bruni, E. Cariati, F. Cariati, F. A. Porta, S. Quici and D. Roberto, Spectrochim. Acta, Part A, 2001, 57, 1417–1426.