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PAPER

Electrochromic second-order NLO chromophores based on M^{II} (M = Ni, Pd, Pt) complexes with diselenolato-dithione (donor-acceptor) ligands[†]

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The donor–acceptor type mixed-ligand complexes $[M(Bz_2pipdt)(dsit)]$; dsit = 2-thioxo-1,3-dithiole-4,5diselenolato (donor); $Bz_2pipdt = 1,4$ -dibenzyl-piperazine-2,3-dithione (acceptor); M(II) = Ni (1), Pd (2), and Pt (3) were prepared and characterized to investigate the variation of the properties by substituting selenium for sulfur in the donor ligand dmit = 2-thioxo-1,3-dithiole-4,5-dithiolato of the corresponding known complexes. Both these classes of complexes exhibit large negative second-order polarizabilities, amongst the highest values determined so far for metal-complexes, and are potential candidates for redox switchability of the molecular first hyperpolarizability due to the bleaching/restoring of the solvatochromic peak for mono-reduction/oxidation. DFT and TD-DFT calculations on 1–3 allow one to correlate geometries and electronic structures and are in agreement with the observed minor changes following the substitution of selenium for sulfur atoms in the dichalcogenolato ligand. The observed differences can be ascribed to the increased size of the selenium atom leading to increased M–X distances and dipolar moments of the ground state, which are highest for the Pd-derivative in the triad.

Introduction

Complexes of d^8 -metals (most often Pt(II)) with non-innocent ligands based on donor–acceptor systems have been deeply investigated for their peculiar electronic properties and are of current interest for their possible use as potential photocatalysts,¹ in solar energy harnessing² and as second-order-non-linear chromophores.³ In square-planar d⁸-metal dithiolene complexes, terminal groups attached to the dithiolene core (C₂S₂MC₂S₂) and

^cDipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Parco Area delle Scienze 17A, 143100 Parma, Italy having different electron withdrawing/donating capability induce a redistribution of the π -electrons in such a way that one of the ligands can be described as a dithione (acceptor), the other one as a dithiolato (donor).⁴ These complexes behave as secondorder non-linear chromophores and show a solvatochromic peak in the visible-near infrared spectral region and remarkably high negative molecular first hyperpolarizability.⁵ The solvatochromic peak is relatable to a HOMO-LUMO transition, where the HOMO is formed by a mixture of metal and dithiolate orbitals while the dithione orbitals give a predominant contribution to the LUMO. A mixed metal/ligand to ligand charge transfer character (MMLL'CT) has been assigned to this transition.⁶ A systematic study on varying the metal,⁶ the dithione and the dithiolato^{7a,b} ligands is in course to highlight the role that each of them plays in affecting the properties of these complexes also with the goal to find the most appealing candidate for secondorder NLO applications. Results of a combined theoretical and experimental study previously performed on the triad [M(II)- $(Bz_2pipdt)(mnt)$ (M(II) = Ni, Pd and Pt; $Bz_2pipdt = 1,4$ -dibenzylpiperazine-2,3-dithione, mnt = maleonitriledithiolato) suggested the platinum compound as the most appealing candidate.⁶ Accordingly we have selected platinum complexes, keeping constant the dithione, Bz₂pipdt, and changing the dithiolato ligand: L = mnt; dcbdt = dicyanobenzodithiolato; dmit = 2-thioxo-1,3dithiole-4,5-dithiolato, see Chart 1.

All these complexes, which are redox active, show large negative second-order polarizability. The observed experimental sequence of $\mu\beta_0$ (×10⁻⁴⁸ esu) = -822 (mnt); -1296 (dcbt); -2011 (dmit) points to the crucial role of the dithiolato ligand in affecting the NLO properties.^{7b} Theoretical studies helped to

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[†] Electronic supplementary information (ESI) available: Fig. S1. Solvatochromic behaviour of [Pt(Bz₂pipdt)(dsit)]; Fig. S2–S5. Electrochemical measurements of [Nit(Bz₂pipdt)(dsit)]; Table S1. Selected experimental and calculated bond distances (Å) and angles (°) for [Ni-(Bz₂pipdt)(dsit)], [Pd(Bz₂pipdt)(dsit)] and [Pt(Bz₂pipdt)(dsit)]. Tables S2–S4. Spatial plots of relevant MOs of [M(Bz₂pipdt)(dsit)] in DMF (M = Ni, Pd, Pt). Table S5. TD-DFT calculated energies and compositions of the lowest lying singlet electronic transitions of [M(Bz₂pipdt)-(dsit)] (M = Ni, Pd, Pt) complexes in DMF. Table S6. Comparison of HOMO–LUMO energy and energy gap between [Pt(Bz₂pipdt)(dnit)] and [Pt(Bz₂pipdt)(dsit)]. Table S7. Calculated ground state dipole moments (μ_g) and $\Delta \mu_{ge}$ of [M(Bz₂pipdt)(dsit)] as former Table S6. CCDC 884915 and 884916. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31537h



explain the high negative second-order polarizability values, which are relatable to a large difference in dipole moments between the excited and the ground state enhanced by the electric field of the solvent and the large oscillator strength for the charge transfer transition which falls at relatively low energy. These factors provide the largest second-order polarizability value to [Pt(Bz₂pipdt)(dmit)]. Building on these studies we have selected dsit = 2-thioxo-1,3-dithiole-4,5-diselenolato where selenium substitutes sulfur in the ligand dmit to further develop the role of the donor, and report here the synthesis, characterization and properties of the triad $[M(Bz_2pipdt)(dsit)], M(II) = Ni$ (1), Pd (2), and Pt (3). To the best of our knowledge X-ray diffractometric studies on 1 and 3 provide the first structural data on d⁸-metal donor/acceptor systems based on dithione/diselenolato ligands. Structural data so far available on d⁸-metal mixed-S/ Se-dichalcogenolene complexes are based on ligands with similar electron-donating properties (extensive π -electron delocalisation inside the C₂S₂MSe₂C₂ core).⁸ Structural data on donor/acceptor systems bearing diselenolato ligands have been previously reported for nickel and platinum diimine-diselenolato complexes.9

Despite the greater size and polarizability of the Se atom compared with the S one, and the crucial contribution of chalcogen atoms of the dichalcogenolato to the HOMO, minor changes in their properties follow the substitution of the chalcogen atoms.

Experimental section

Chemicals

Reagents and solvents of Reagent Grade and Spectroscopic Grade (DMF, CH_3CN and CS_2) have been used as received from Aldrich.

Preparation

[Ni(Bz₂pipdt)(dsit)] (1). (Bu₄N)₂[Ni(dsit)₂] (50.00 mg) in 25 cm³ of CH₃CN (green solution) was added dropwise to a blue solution of [Ni(Bz₂pipdt)Cl₂] (94.85 mg) in 25 cm³ CH₃CN, under stirring and reflux. After one day a blue solid was formed (48.44 mg; yield: 85%). This solid was filtered, washed with diethyl ether and then dried. Well formed crystals suitable for X-ray crystallography have been obtained through re-crystallization from DMF–diethyl ether. Analytical results are in accordance with the formula [Ni(Bz₂pipdt)(dsit)]. Calculated for C₂₁H₁₈N₂NiS₅Se₂: C, 37.35; H, 2.69; N, 4.15; S, 23.74. Found: C, 37.6; H, 2.6; N, 4.1; S, 22.4. IR spectra, KBr pellets, wavenumbers (cm⁻¹): 3055 vw, 2933 vw, 1509 s, 1447 w, 1431 m, 1342 s, 1307 vw, 1261 m, 1238 vw, 1180 m, 1060 vs, 975 vw, 959 vw, 905 vw, 882 vw, 859 vw, 797 vw, 732 m, 689 m, 662 w, 631 w, 573 w, 503 m, 441 m, 422 w. [Pd(Bz₂pipdt)(dsit)] (2). Compound 2 has been prepared as reported above for the corresponding Ni complex using the following amounts: 70.01 mg of $(Bu_4N)_2[Ni(dsit)_2]$ in 25 cm³ CH₃CN and 156.18 mg of [Pd(Bz₂pipdt)Cl₂] in 25 cm³ of CH₃CN; 71.43 mg of a green solid have been obtained (yield: 82%). Analytical results are in accordance with the formula [Pd(Bz₂pipdt)(dsit)]. Calculated for C₂₁H₁₈N₂PdS₅Se₂: C, 34.88; H, 2.51; N, 3.87; S, 21.84. Found: C, 35.0; H, 2.6; N, 3.8; S, 21.2. IR spectra, KBr pellets, wavenumbers (cm⁻¹): 3081 vw, 3058 vw, 3030 vw, 2954 vw, 2941 vw, 2917 vw, 1516 vs, 1450 m, 1435 m, 1365 s, 1342 s, 1303 vw, 1268 m, 1237 vw, 1184 w, 1110 vw, 1056 vs, 1029 vw, 979 vw, 882 vw, 797 vw, 727 m, 696 m, 665 vw, 627 vw, 569 vw, 546 vw, 507 m, 445 m, 422 s.

[Pt(Bz₂pipdt)(dsit)] (3). Compound 3 has been prepared as reported above for the corresponding Ni complex using the following amounts: 112.89 mg of $(Bu_4N)_2[Ni(dsit)_2]$ in 25 cm³ CH₃CN and 50.00 mg of [Pt(Bz₂pipdt)Cl₂] in 25 cm³ of CH₃CN; 62.77 mg of a green solid have been obtained (yield: 89%). Well formed crystals suitable for X-ray crystallography have been obtained through re-crystallization from DMF–diethyl ether. Analytical results are in accordance with the formula [Pt-(Bz₂pipdt)(dsit)]. Calculated for C₂₁H₁₈N₂PtS₅Se₂: C, 31.07; H, 2.24; N, 3.45; S, 19.75. Found: C, 30.8; H, 2.1; N, 3.3; S, 18.8. IR spectra, KBr pellets, wavenumbers (cm⁻¹): 3062 vw, 2920 vw, 1515 vs, 1454 m, 1429 m, 1332 vs, 1307 vw, 1267 w, 1190 vw, 1059 vs, 1028 vw, 977 vw, 734 w, 698 w, 633 w, 511 w, 500 w, 424 w.

Microanalyses were performed by means of a Carlo Erba CHNS Elemental Analyzer model EA1108.

Spectroscopic and electrochemical measurements

IR 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* spectro-photometer. 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 the counter-electrode and Ag/AgCl in saturated KCl solution as the reference electrode. The experiments were performed at room temperature (25 °C), in dry and argon-degassed DMF containing 0.1 mol dm⁻³ Bu₄NPF₆ as the supporting electrolyte, at 25–200 mV s⁻¹ scan rate.

Spectroelectrochemistry measurements have been performed at room temperature by the optically transparent thin layer electrochemistry technique (OTTLE) in dry and argon-degassed DMF containing 0.1 mol dm⁻³ Bu₄NPF₆ as the supporting electrolyte using a 0.5 mm quartz cell at -0.50 and +0.1 V for the reduction and oxidation process, respectively. The UV-Vis-NIR spectra have been recorded with a *Jasco V-670* spectrophotometer.

NLO measurements

 $EFISH^{10a-c}$ experiments have been performed using a freshly prepared 10^{-3} M solution in DMF (chosen in order to avoid any possible aggregation of the chromophores and to guarantee

enough solubility to ensure the accuracy of the measurement) 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 has been used to obtain the Maker fringe pattern (harmonic intensity variation as a function of liquid cell translation). In the EFISH experiments the incident beam has been 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 have been determined (assumed to be real because the imaginary part has been neglected) from the experimental value $\gamma_{\rm EFISH}$, 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 $\mu\beta_{\lambda}(-2\omega; \omega, \omega)/5kT$, μ is the ground state dipole moment, and β_{λ} is the projection along the dipole moment direction of the vectorial component β_{vec} of the tensorial quadratic hyperpolarizability working with the incident wavelength λ . The EFISH experiment has been performed as follows. First the second order response of the pure solvent, then the second order response of the chromophore solution, and finally the solvent again have been recorded. The EFISH values reported in Table 2 are the average of twelve successive measurements performed on the same sample, each compared to the previous and to the following solvent. All experimental EFISH $\beta_{\lambda||0}$ values are defined according to the "phenomenological" convention.^{10d}

Data collection and structure determination

A summary of data collection and structure refinement for [Ni-(Bz₂pipdt)(dsit)] (1) and [Pt(Bz₂pipdt)(dsit)] (3) 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 data were integrated from several series of exposures frames (0.3° width) covering the sphere of reciprocal space.¹¹ An absorption correction was applied using the program SADABS¹² with min. and max. transmission factors of 0.773 and 1.000 (1), 0.601 and 1.000 (3). The structures were solved by direct methods (SIR2004¹³) and refined on F^2 with full-matrix least squares (SHELXL-97¹⁴), using the Wingx software package.¹⁵

For both compounds, non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed at their calculated positions. Graphical material was prepared with the Mercury 2.0¹⁶ and ORTEP3 for Windows¹⁷ programs. CCDC 884915 and 884916 contain the supplementary crystallographic data for this paper.

Computational details

The electronic properties of the $[M(Bz_2pipdt)(dsit)]$ complexes (M = Ni, Pd, Pt) were investigated by means of DFT methods.¹⁸ The molecular structures of the complexes were optimized starting from the X-ray experimental geometry of $[Pt(Bz_2pipdt)-(dsit)]$ using no symmetry constraints. The Becke three-parameter exchange functional with the Lee–Yang–Parr

 Table 1
 Summary of X-ray crystallographic data for [Ni(Bz₂pipdt) (dsit)] (1) and [Pt(Bz₂pipdt)(dsit)] (3)

_	[Ni(Bz ₂ pipdt)(dsit)] (1)	(dsit) (1) [Pt(Bz ₂ pipdt)(dsit)] (3)			
Empirical formula Formula weight Color, habit Crystal size (mm) Crystal system Space group <i>a</i> (Å) <i>b</i> (Å) <i>c</i> (Å) α (°) β (°) γ (°) V (Å ³) <i>Z</i> <i>T</i> (K) ρ (calc) (Mg m ⁻³) μ (mm ⁻¹) θ range (°) No. of rflcn/unique GooF <i>P</i> .	$\begin{array}{c} C_{21}H_{18}N_2NiS_5Se_2\\ 675.30\\ Brown, plate\\ 0.13 \times 0.11 \times 0.05\\ Monoclinic\\ P2_1/n\\ 9.256(1)\\ 23.119(2)\\ 11.503(1)\\ 90\\ 98.741(2)\\ 90\\ 2432.9(4)\\ 4\\ 293(2)\\ 1.844\\ 4.232\\ 1.76 \text{ to } 26.16\\ 29 067/4861\\ 1.006\\ 0.0419\\ \end{array}$	$\begin{array}{c} C_{21}H_{18}N_2PtS_5Se_2\\ 811.68\\ Brown, block\\ 0.18 \times 0.17 \times 0.11\\ Monoclinic\\ P2_1/n\\ 9.267(2)\\ 23.189(5)\\ 11.555(3)\\ 90\\ 98.069(4)\\ 90\\ 2459(1)\\ 4\\ 293(2)\\ 2.193\\ 9.107\\ 1.76 \text{ to } 27.66\\ 32 475/5703\\ 1.017\\ 0.0426\end{array}$			
wR_2	0.0728	0.0909			

Table 2 Optical and EFISH* results for [M(Bz₂pipdt)(dsit)] complexes. Values for corresponding dmit⁷ are reported for comparison reasons

Complex [M(Bz ₂ pipdt)(dsit)] 1–3 [M(Bz ₂ pipdt)(dmit)] 1a–3a		$\lambda_{\max}{}^{a}$ (nm)	$\varepsilon^{a} (\times 10^{-3} \mathrm{mol}^{-1} \mathrm{dm}^{3} \mathrm{cm}^{-1})$	$\mu\beta^{a,b} (10^{-48} \text{ esu})$	$\mu\beta_0 \ (10^{-48} \ \mathrm{esu})$	
Ni	1	840	9.2	-5330	-962	
	1a	858	10.6	-6100	-926	
Pd	2	812	6.0	-4950	-1114	
	2a	819	11.3	-5360	-1146	
Pt	3	803	9.4	-4400	-1053	
	3a	827	14.8	-1000	-2011	

^a In DMF. ^b Average value of twelve successive measurements, the uncertainty of the measure is between ± 3 and $\pm 5.5\%$.

correlation functional (B3LYP)^{19,20} was employed together with the 6-311G(d,p) basis set^{21,22} for the C, H, N, and S atoms. The Ni, Pd, Pt, and Se atoms were treated with the SDD valence basis set²³⁻²⁵ and with the MDF10 (Ni), MWB28 (Pd, Se), and MWB60 (Pt) effective core potentials. An additional d polarization function was employed for selenium.²⁶ Single point calculations were performed using the same basis set employed for the calculation for the metal atoms and Se, whereas C, H, N, and S atoms were treated with the 6-311G(d,p) basis set.²⁷ To address DMF solvation effects, the conductor-like screening model as developed in the polarisable continuum model (CPCM)²⁸ has been applied with united atom topological model atomic radii.²⁹ Single point CPCM calculations of the complexes were performed using gas-phase optimized geometries. TD-DFT^{30,31} 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). All the calculations were performed with the Gaussian 03 program suite.³² GaussView was used to generate molecular orbitals.³³ AOMix was used for determining atomic orbital compositions employing Mulliken population analysis,³⁴ and SWizard³⁵ was used to analyze the electronic transitions obtained from TD-DFT calculations.

Results and discussion

Synthesis

 $[M(II)(Bz_2pipdt)(dsit)]$ [M(II) = Ni (1); Pd (2); Pt (3)] have been obtained by reacting $[M(II)(Bz_2pipdt)Cl_2]$ with $(Bu_4N)_2[Ni(II)-(dsit)_2]^{36}$ following the same procedure used for the preparation of the corresponding dmit complexes,^{7a} as shown in Scheme 1.

Salts of nickel dianionic complexes provide the required dianion, which when uncoordinated is less stable, to form the desired mixed-ligand complexes in high yields (80-90%) with respect to the [M(Bz₂pipdt)Cl₂] reagent, accompanied by Bu₄NCl and degradation products containing the nickel cations. On slow evaporation of the solvent, well formed dark crystals precipitated.

X-ray structures

Compounds 1 and 3 crystallize in the monoclinic P21/n space group and are isostructural, for this reason only the molecular structure of 3 will be described in detail. The molecular drawing of 3 is depicted in Fig. 1. In 3 two sulfur and two selenium atoms from the Bz₂pipdt and dsit ligands, respectively, define the coordination environment of the metals, which is in a slightly distorted square planar geometry. As reported in Table S1,† the







Fig. 1 Ortep drawing of $[Pt(Bz_2pipdt)(dsit)]$ (3) with thermal ellipsoids drawn at the 30% probability level.



Fig. 2 Crystal packing of $[Pt(Bz_2pipdt)(dsit)]$ (3). Partial π -stacks are depicted by dashed bonds.

CC bond distances involving the dsit ligand are shorter than those originating from Bz₂pipdt, in agreement with the prevailing diselenolato character for dsit and dithione character for Bz₂pipdt. This is also reflected in the C–S distances of the Bz₂pipdt ligands (range 1.673(5)–1.700(6) Å), as they are in agreement with a dithione structure.^{5–7,36} The crystal packing of **3** is reported in Fig. 2. The Pt atoms are located between one of the CH₂ groups and an aromatic CH group of two symmetry related Bz₂pipdt ligands. Moreover, the presence of an extensive net of π -stacks between the aromatic rings of the Bz₂pipdt ligands determines the formation of layers that are parallel to the *ac* plane. Those layers interact with each other by means of very weak π - π interactions of the Bz₂pipdt ligands with the minimum distance occurring between C(101) and C(61)' atoms (3.83(1) Å, symmetry code' = -x; -y; -z).

Visible absorption spectroscopy and EFISH data

Complexes 1–3 are characterized by a broad absorption in the visible region with medium molar absorption coefficients reported in Table 2, and a negative solvatochromism, as shown in Fig. S1[†] as an example for 3. The energy of the solvatochromic peaks 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.^{38a} 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.^{6,37,38b} 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 1064 nm emission of a Q-switched Nd:YAG laser in a high pressure hydrogen cell (60 bar), as described in detail in the Experimental section. The setup used allows the determination of the scalar product $\mu\beta_{\lambda}$ ($\mu =$ ground state dipole moment; $\beta_{\lambda} =$ 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 by applying the equation $\beta_0 = \beta_{\lambda} [1 - (2\lambda \max/\lambda)^2] [1 - (\lambda \max/\lambda)^2]$. These values are collected in Table 2.

Electrochemistry

Cyclic voltammetric experiments performed on DMF solutions of the complex exhibit two reversible reduction waves and one irreversible oxidation wave as reported in Table 3.

The reduction processes, see CV scans in Fig. 3 as a representative example for 1 and Fig. S2 and S3,† show reduction values close to those found for other mixed-ligand complexes bearing R_2 pipdt ligands.^{6–8}

The oxidation potential (E_a), which is sensitive to the nature of the donor dichalcogenolato ligand, falls between those of dmit^{7a} and of mnt,³⁹ suggesting a similar sequence for the ease

Table 3 Cyclic voltammetric data. Measured at the Pt electrode in DMF, 0.1 M Bu₄NPF₆, scan rate 100 mV s⁻¹ (reference electrode Ag/AgCl)

[M(Bz, pindt)	$F(V)^a$	$F^1 \dots (V)^b$	$F^2 = (V)^b$
(dsit)]	$D_a(V) \rightarrow 1+$	$0 \rightleftharpoons 1-$	$1 \rightarrow \neq 2 \rightarrow 2 \rightarrow$
Ni	+0.86	-0.39	-0.84
Pd	+0.69	-0.41	-0.91
Pt	+0.65	-0.49	-1.04

^{*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 ip_{red}/ip_{ox} close to unity).



Fig. 3 Cyclic voltammograms of 1 recorded at 298 K with different scan rates in a DMF solution containing 0.1 M Bu_4NPF_6 .



Fig. 4 Spectro-electrochemical experiments on $[Pt(Bz_2pipdt)(dsit)]$ in 0.1 M Bu₄NPF₆–DMF at room temperature (298 K). The potential was held at -0.5 V vs. Ag/AgCl.

of one electron removal which can be related to the donor capacity of the ligand.

Electrochemical results are consistent with theoretical results (see related discussion in next section), which show that the ligand acting as dithione gives a prevalent contribution to the LUMO (relatable to reduction processes) and the ligand acting as dichalcogenolato 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 reversible nature of the first reduction process, verified by the variable scan rate cyclic voltammetry (see Fig. S4 and S5⁺), allowed a spectroelectrochemical investigation. The formation of the monoreduced species (Fig. 4) is accompanied by a change of the electronic spectrum with depletion of the solvatochromic peak, which can be restored during the oxidation process. A reduction in intensity and a small shift to higher energy of the HOMO-LUMO transition at 827 nm are typical for monoreduced metal-bis-1,2dithiolene complexes.⁴

These results suggest that these redox active chromophores can be of interest for redox switching of the nonlinear optical response⁴⁰ useful for applications in optical devices although suitable processing of these complexes⁴¹ is required for the realization of a molecular optical switch.

Theoretical studies

The electronic properties of complexes were investigated by means of DFT methods in order to evaluate the influence of the Se atom of dsit in place of the S of the corresponding dmit complexes previously investigated^{7b} and of the metal center (Ni, Pd, and Pt). The molecular structures of the complexes of formula $[M(Bz_2pipdt)(dsit)]$ were optimized starting from the experimental geometry of $[Pt(Bz_2pipdt)(dsit)]$. In general there is good agreement between the DFT-optimized and experimental geometries, even though, for all complexes, the M–S/Se bond distances are slightly overestimated, see Table S1.[†] The electronic structures of the complexes were evaluated both in vacuum and by

Table 4 Spatial plots of HOMO and LUMO (isovalue = 0.04) of [M(Bz₂pipdt)(dsit)] (M = Ni, Pd, Pt) in the gas-phase and in DMF (B3LYP/6-311G (d,p)-SDD), together with the contribution of different fragments to these orbitals

	Ni				Pd				Pt			
	E (eV)	<i>E</i> (eV) Fragment composition		on (%)	E (eV)	Fragment composition (%)		E (eV)	Fragment composition (%)			
		Ni	Bz ₂ pipdt	dsit		Pd	Bz ₂ pipdt	dsit		Pt	Bz ₂ pipdt	dsit
	Gas-phase				Gas-phase			Gas-phase				
LUMO HOMO HOMO–LUMO gap	-3.66 -4.97 1.31	4.4 3.6	72.5 25.1	23.1 71.4	-3.73 -4.92 1.19	3.5 3.5	74.9 22.9	21.7 73.5	-3.69 -4.99 1.30	6.0 4.2	71.2 26.3	22.8 69.5
	DMF-pł	nase			DMF-pl	nase			DMF-pł	nase		
LUMO HOMO HOMO–LUMO gap	-3.68 -5.34 1.66	2.8 6.4	87.2 13.9	10.0 74.8	-3.75 -5.30 1.55	2.4 5.9	89.1 11.6	8.5 82.5	-3.74 -5.32 1.58	4.3 7.9	85.2 16.8	10.6 75.3



Fig. 5 Percentage contributions of different atoms to frontiers molecular orbitals of [M(Bz₂pipdt)(dsit)] (HOMO, below and LUMO, above). CPCM (DMF) B3LYP/6-311G(d,p)-SDDv.

taking into account the contribution of the solvent (DMF) by means of the CPCM method. The energies along with the contour plots of the frontier orbitals of [M(Bz₂pipdt)(dsit)] calculated in DMF and evaluated in the gas-phase for the sake of completeness are reported in Tables 4 and S2–S4.† In all cases the HOMO and LUMO are both formed from the out-of-plane antibonding interactions between the metal's d_{xz} orbital and ligand based C_2X_2 (X = S and Se) orbitals (with C–C π and C– X π^* character). As previously found for [Pt(Bz₂pipdt)(dithiolato)],^{7b} the HOMO is mainly located on the dichalcogenolato ligand, whereas the LUMO mainly derives from the dithione ligand. The contribution of three molecular fragments (metal, dsit, Bz₂pipdt) to the frontier molecular orbitals is depicted in Fig. 5. The HOMO is at least 75% derived from the dsit ligand, whereas the dithione ligand contributes at least 85% to the LUMO.

Furthermore, the degree of localization of the HOMO and LUMO on the dsit and Bz₂pipdt ligands, respectively, varies in



Fig. 6 Energy levels of frontier HOMO and LUMO of $[M(Bz_2pipdt)-(dsit)]$ (1–3) complexes (M = Ni, Pd, Pt) calculated in the gas-phase and in DMF (CPCM).

the order Pt < Ni < Pd (see Tables 4 and S2–S4[†]). In Fig. 6 a comparison between the HOMO–LUMO energy gap calculated

for the gas phase and in DMF for the three complexes is reported. It can be appreciated how the presence of a polar solvent such as DMF imparts considerable stabilization on the HOMO, whereas the LUMO is only marginally affected. The influence of the selenium atom in dsit can be evaluated by comparing the properties of the frontier orbitals of [Pt(Bz₂pipdt)-(dsit)] and [Pt(Bz₂pipdt)(dmit)].^{7b} The fragmental composition of the HOMO and LUMO orbitals is very similar, but the HOMO is stabilized by 0.06 eV in [Pt(Bz₂pipdt)(dsit)] when compared to [Pt(Bz₂pipdt)(dmit)] (see Table S6†).

This stabilization can be ascribed to the presence of the Se atom in place of S. The greater Pt–Se bond distances with respect to Pt– S (~0.1 Å) can have a stabilizing influence on the HOMO according to the fact that this orbital is mainly localized on the dsit/dmit ligand system and is characterized by π -antibonding character.

According to the shapes of the frontier orbitals, and as found for strictly related complexes,^{5–7} it can be inferred that the HOMO–LUMO transition will have mixed metal–ligand to metal–ligand character (MMLL'CT). Vertical excitation energies of the three complexes **1–3** were determined using timedependent density functional theory (TD-DFT) in DMF as the solvent. The first five singlet–singlet excitation energies are reported in Table S5.[†] For all complexes, the first transition is characterized by the greater oscillator strength and is mainly comprised of a HOMO to LUMO excitation, supporting its assignment as the MMLL'CT transition. There is a qualitative agreement between the calculated first singlet–singlet transition in DMF and the experimental results, even though the calculation overestimates the λ_{max} by more than 100 nm.

The negative solvatochromism of these complexes can also be inferred by the negative value of the $\Delta \mu_{ge}$ which is approximately -8.5 D for the Ni and Pt complexes and -10.3 for the Pd one. In Table S7† the calculated ground state dipole moments (μ_g) and $\Delta \mu_{ge}$ of [M(Bz₂pipdt)(dsit)] are listed.

A different sequence of $\mu\beta_0$ values for the dsit (Pd \geq Pt)/dmit (Pt > Pd) derivatives is observed. By taking into account a simplified two-state model⁴² the second-order polarizability is given by

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

A slightly lower E_{max} value and a higher $\Delta \mu_{\text{ge}}$ value for Pdversus Pt-dsit derivatives may explain the observed sequence.

Conclusions and perspectives

New diselenolato–dithione M(II) (M = Ni, Pd, Pt) redox-active, electrochromic chromophores showing second-order NLO response have been synthesized and studied experimentally and theoretically in order to elucidate the properties and electronic structure of these complexes and to reach structure–property relationships which are crucial to design optimal candidates for NLO applications. In particular the comparison of the dithioand diseleno-lato corresponding triads allows the conclusion that, despite the greater size and polarizability of the Se atom compared with the S one, and of the crucial contribution of chalcogen atoms of the dichalcogenolato to the HOMO, the properties of the two classes of complexes are similar and only minor changes follow the substitution of the chalcogen atoms. Both these classes of complexes exhibit large negative second-order polarizabilities, amongst the highest values determined so far for metal-complexes, and, due to the bleaching/ restoring of the solvatochromic peak for mono-reduction/ oxidation, are potential candidates for redox switchability of the second-order NLO response, given suitable processing of these complexes.

It is noteworthy that 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 diselenolato ligand, whereas it does not affect significantly the LUMO, which is mainly localized on the dithione, in agreement with experimental data.

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