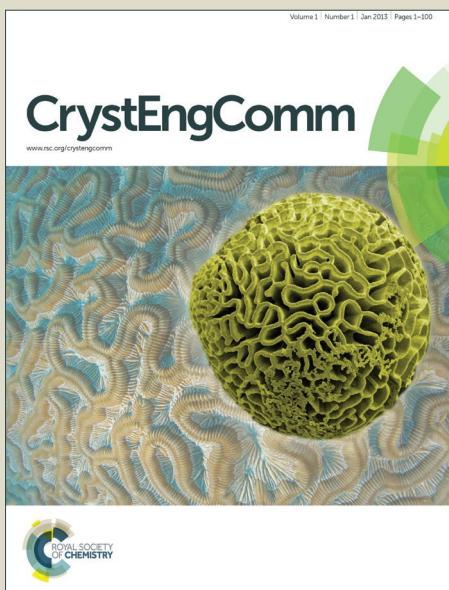


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ARTICLE TYPE

Structural changes in M^{II} dithione/dithiolato complexes (M = Ni, Pd, Pt) on varying the dithione functionalization

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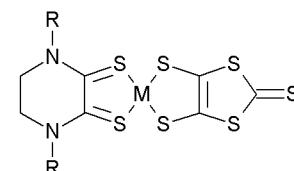
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The Ni triad [M(R₂pipdt)(dmit)] based on donor/acceptor S,S' ligands, where R₂pipdt = 1,4-diisopropyl-piperazine-2,3-dithione (acceptor) and dmit = 2-thioxo-1,3-dithiole-4,5-dithiolato (donor), was completed by preparing and characterizing the Pd(**2**) and Pt(**3**) compounds in addition to the already known Ni(**1**) complex. The rationale behind the work was to compare the properties and structures inside the triad and with those of the corresponding Ni(**4**), Pd(**5**) and Pt(**6**) complexes where R = Bz. Minor changes in the properties as redox active nonlinear second-order (NLO) chromophores were observed in solution for the two triads. Instead, different structural features, reflected by changes in the diffuse reflectance spectra, were observed in their crystals on changing R from Bz to Prⁱ in the piperazine ring and also, more surprisingly, inside the triads. **2** (isostructural with **1**) and **3** crystallized in monoclinic *P*2₁/n and orthorhombic *P*bca space groups, respectively. The crystal packings of **2** and **3** are also markedly different. In particular **1** and **2** form head-to-tail dimers whereas **3** forms supramolecular layers characterized by a partial stack between the molecular planes. Large differences in the crystal structures, induced by diverse number and types of interactions exchanged by the peripheral fragments of the ligands, were found in the Bz-triad. Indeed, the molecules are stacked in a head-to-head and in a head-to-tail fashion in **4** and in **5/6**, respectively. Moreover, significantly different packings were observed. The Hirshfeld surface analysis was used to provide a detailed description of the main types of interactions involved in the crystal packing of the six complexes.

Introduction

Square-planar d⁸ metal dithiolene complexes have been intensely investigated for their peculiar properties of interest in the fields of molecular materials exhibiting optical, conducting and magnetic properties.¹ The electronic properties of dithiolene complexes can be tuned by variation of substituents at the dithiolene core, and these terminal groups affect the highly delocalized frontier orbitals and related properties. In particular terminal groups attached to the dithiolene core with 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). This behaviour is similar to what happens in the metal d⁸ diimine-dithiolato complexes, where the acceptor is the diimine ligand.² These complexes behave as redox active second-order nonlinear chromophores showing high negative molecular first hyperpolarizability.^{1d,3,4} An extensive experimental/theoretical investigation by our group by systematically varying the metal,^{3,4} the dithione⁴ and the dithiolato³ ligands has allowed to highlight the role that each component, i.e. donor, acceptor and metal ion, plays in tuning the properties of these complexes at molecular level. It is found that mixed ligand complexes based on dithione

(R₂pipdt = 1,4-dibenzyl-piperazine-2,3-dithione) and dithiolate ligands (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolato) represent optimal candidates to achieve high second order NLO activity (See Scheme 1). Moreover, open-shell and closed-shell metal-dmit complexes with similar ligands can form near infrared pigments, conducting or magnetic materials. In these systems the intermolecular interactions and stacking patterns govern the nature of these materials.⁵



R₂pipdt dmit

R = Prⁱ; M = Ni (**1**); Pd (**2**); Pt (**3**)
R = Bz; M = Ni (**4**); Pd (**5**); Pt (**6**)

Scheme 1

Given the relevance of intermolecular interactions in determining stacking patterns and related properties, we address this study mainly to point out the structural features of [M(Prⁱ2pipdt)(dmit)]

[Pr^{i} = isopropyl; M(II) = Ni (**1**), previously reported,⁶ Pd (**2**); and Pt (**3**) properties when compared to the corresponding complexes bearing Bz groups on the piperazine ring of the acceptor ligand, [$\text{M}(\text{Bz}_2\text{pipdt})(\text{dmit})$] (Bz: benzyl; M(II) = Ni (**4**),⁶ Pd (**5**),^{3e} and Pt (**6**)).^{3e} The properties of these complexes are also compared in solution to support a predictable similar behaviour. Due to difficulties encountered in obtaining Pd and Pt compounds, as generally found when using the same synthetic procedure to prepare nickel-dithiolenes,¹⁴ the influence of these substituents has been investigated previously for the nickel derivatives alone.⁶ It was observed that when the Bz group⁶ is present, the molecules are stacked in a one-dimensional columnar structure. Instead, in the Pr^{i} case,^{3a} the Ni complex units are arranged head-to-tail forming dimmers. Since palladium and platinum derivatives are currently available through an effective different synthetic procedure, it seemed interesting to us to deepen this investigation enlarging the comparison of crystal packing features on **1-6**. The Hirshfeld surface (HS) analysis⁷ is an appropriate tool to investigate the packing features of an homologous series of compounds, and was employed to perform a thorough comparison of the packing in the six complexes, pointing out the different types of interactions between the two [$\text{M}(\text{Bz}_2\text{pipdt})(\text{dmit})$]/[$\text{M}(\text{Pr}^{\text{i}}_2\text{pipdt})(\text{dmit})$] triads and inside each one of them.

25 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.

30 Preparations.

[Ni($\text{Pr}^{\text{i}}_2\text{pipdt}$)(dmit)] (**1**). **1** has been prepared following a procedure described in ref. 1d.

[Pd($\text{Pr}^{\text{i}}_2\text{pipdt}$)(dmit)] (**2**). ($n\text{-Bu}_4\text{N}$)₂[Ni(dmit)₂] (114.83 mg) in 25 cm³ of CH_3CN , green solution, was added dropwise to [Pd($\text{Pr}^{\text{i}}_2\text{pipdt}$)](Cl)₂ (50.01 mg) in 25 cm³ CH_3CN , dark red suspension, under stirring. The solution, which turned to dark green immediately, was left under reflux for 24h after that a precipitate was formed. The dark green precipitate was filtered, washed with diethyl ether, dried and recrystallized from DMF/diethyl ether (yield: 61.67 mg, 87%) CHNS: Found (Calcd for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{PdS}_7$) C% 29.77 (29.28), H% 3.38 (3.40), N% 5.17 (5.25) S% 44.53 (42.10). FT-IR spectrum (cm⁻¹) 2928vw, 2206vs, 2187vw, 1635m, 1528vs, 1497vw, 1464w, 1454w, 1437m, 1357m, 1263w, 1184m, 1149w, 1109w, 1081w, 862vw, 738m, 698m, 605vw, 574w, 548w, 511w, 471w.

[Pt($\text{Pr}^{\text{i}}_2\text{pipdt}$)(dmit)] (**3**). ($n\text{-Bu}_4\text{N}$)₂[Ni(dmit)₂] (107.28 mg) in 25 cm³ of CH_3CN , green solution, was added dropwise to [Pt($\text{Pr}^{\text{i}}_2\text{pipdt}$)](Cl)₂ (50.00 mg) in 25 cm³ CH_3CN , dark red suspension, under stirring. The solution, which turned to dark green immediately, was left under reflux for 24h after that a precipitate was formed. The dark green precipitate was filtered, washed with diethyl ether, dried and recrystallized from DMF/diethyl ether. Recrystallization from DMF/ diethyl ether (yield: 66.64 mg, 94%) CHNS: Found (Calcd for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{PtS}_7$) C% 25.39 (25.11); H% 2.46 (2.92); N% 4.50 (4.51); S% 39.14 (36.09). FT-IR spectrum (cm⁻¹) 2967vw, 2927vw, 1645vs,

1508vs, 1428vs, 1378m, 1356m, 1276w, 1251w, 1240w, 1190w, 1108s, 1049s, 1024s, 904m, 720w, 587w, 511w, 475w.

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

Spectroscopic and Electrochemical Measurements. 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* spectro-photometer. Cyclic voltammograms were carried out on a *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 Bu_4NBF_4 as supporting electrolyte, in the 20-100 mV s⁻¹ scan rate range.

NLO Measurements. EFISH 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 (50 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 thickness of liquid traversed). In the EFISH experiments the incident beam (6 ns pulses with 10 Hz repetition rate) has been synchronized with a DC field applied to the solution (5 μs duration) 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 γ_{EFISH} , through equation (2):

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

where λ_{EFISH} is the sum of a cubic electronic contribution $\gamma(-2\omega; \omega, \omega, 0)$, which is neglected, and of a quadratic orientational contribution $\mu\beta\lambda(-2\omega; \omega, \omega)/5kT$, being μ 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 .

X-ray Data Collection and Structure Determination.

A summary of data collection and structure refinement for [Pd($\text{Pr}^{\text{i}}_2\text{pipdt}$)(dmit)] (**2**) and [Pt($\text{Pr}^{\text{i}}_2\text{pipdt}$)(dmit)] (**3**) is reported in Table 1. Single crystal data were collected with a *Bruker Smart 1000* 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 zone of reciprocal lattice. The intensity data were integrated from several series of exposures frames (0.3° width) covering the sphere of reciprocal space.⁸ An absorption correction was applied using the program SADABS⁹ with min. and max. transmission factors of: 0.856-1.000 (**2**) and 0.487-1.000 (**3**). The structure was solved by direct methods (SIR97¹⁰) and refined on F^2 with full-matrix least squares (SHELXL-97¹¹), using the Wingx software package.^{12,13} Non hydrogen atoms were refined anisotropically and the hydrogen atoms were placed at their calculated positions.

Graphical material was prepared with the Mercury 3.0¹⁴ program. CCDC 1040215-1040216 contain the supplementary crystallographic data for this paper.

⁵ Hirshfeld surface analysis

The Hirshfeld surface (HS) properties^{7, 15} were computed with the CrystalExplorer 3.0 program¹⁶ in order to elucidate the differences and similarities between the packing modes for the six complexes. The HS defines the volume of space in a crystal where the sum of the electron density of spherical atom for the molecule (pro-molecule) exceeds that for the crystal (pro-crystal). Various properties of the HS can be computed and visualized, in particular d_e and d_i , which represent the distance from a point on the surface to the nearest nucleus outside or inside, respectively, ¹⁵ the surface. The d_{norm} is the normalized contact distance and is defined by taking into account d_e and d_i and the van der Waals radii of the atoms:

$$d_{norm} = \frac{d_i - r_i^{vdW}}{r_i^{vdW}} + \frac{d_e - r_e^{vdW}}{r_e^{vdW}}$$

d_{norm} can be mapped on the HS providing clear evidences of the interactions exchanged by adjacent molecular fragment (visualized as red spots on the HS). Moreover, the correlation between d_e and d_i provides the fingerprint plots, which are 2D diagrams that provide a thorough depiction of the overall interactions exchanged by the molecules within the crystal.¹⁷

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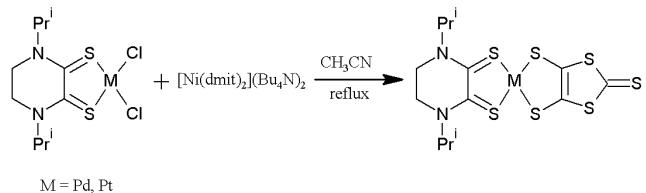
Table 1 Summary of X-ray crystallographic data for [Pd(Prⁱ₂pipdt)(dmit)] (**2**) and [Pt(Prⁱ₂pipdt)(dmit)] (**3**).

	[Pd(Pr ⁱ ₂ pipdt)(dmit)]	[Pt(Pr ⁱ ₂ pipdt)(dmit)]
Empirical formula	C ₁₃ H ₁₈ N ₂ PdS ₇	C ₁₃ H ₁₈ N ₂ PtS ₇
Formula weight	533.11	621.80
Crystal size (mm)	0.20 x 0.15 x 0.10	0.32 x 0.12 x 0.10
Crystal system	Monoclinic	Orthorhombic
Space group	P2 ₁ /n	Pbca
a, b, c (Å)	9.687(2), 17.320(5), 12.544(3)	14.578(1), 16.218(1), 16.257(1)
α, β, γ(deg.)	90, 108.034(7), 90	90, 90, 90
V (Å³)	2001.2(9)	3843.6(4)
Z	4	8
T (K)	293 (2)	200(2)
ρ(calc) (Mg/m³)	1.769	2.149
μ (mm⁻¹)	1.656	8.060
θ range (deg.)	2.07 to 28.03	2.26 to 27.03
No. of rflen/obsv (I>2σ(I))	24254 / 4810	41982 / 4218
GooF	1.005	1.009
R1 [a]	0.0289	0.0294
wR2 [b]	0.0673	0.0641

^a R1 = $\sum ||F_O| - |F_C|| / \sum |F_O|$; [b] wR2 = $[\sum [w(F_O^2 - F_C^2)^2] / \sum [w(F_O^2)^2]]^{1/2}$, $w = 1 / [\sigma^2(F_O^2) + (aP)^2 + bP]$, where P = $[\max(F_O^2, 0) + 2F_C^2]/3$.

Results and Discussion

Synthesis. [M(II)(Prⁱ₂pipdt)(dmit)], [M(II) = Pd (**2**); Pt (**3**)] have been obtained by reacting [M(II)(Prⁱ₂pipdt)Cl₂] with (Bu₄N)₂[Ni(II)(dmit)₂] as shown in Scheme 2:

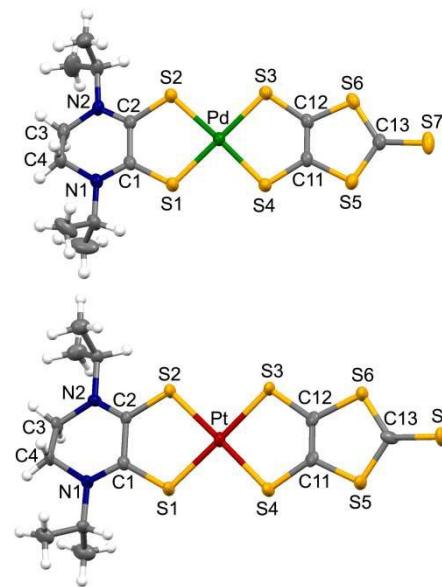


Scheme 2

Salts of nickel dianionic complexes provide the required dianion, which when uncoordinated is less stable, to form the desired ⁴⁰ mixed-ligand complexes in high yields (80-90%) with respect to the [M(Prⁱ₂pipdt)Cl₂] reagent, accompanied with Bu₄NCl and degradation products containing the nickel cations. On slow evaporation of the solvents, well-formed dark crystals precipitated.

⁴⁵ X-ray structures.

The molecular structures of [Pd(Prⁱ₂pipdt)(dmit)] (**2**) and [Pt(Prⁱ₂pipdt)(dmit)] (**3**) are reported in Figure 1. Despite the very similar molecular structures the two compounds crystallize in different space groups, monoclinic P2₁/n for **2** and orthorhombic ⁵⁰ Pbca for **3**. The metal geometry is square planar according to the presence of four sulphur atoms from two S,S bidentate ligands. The geometry of **2** and **3** is more regular than that reported for strictly related compounds, namely [Pd(Me₂pipdt)(dmit)]¹⁸ [Pd(Bz₂pipdt)(dmit)] and [Pt(Bz₂pipdt)(dmit)]^{3e}, in which the dihedral angle between the *dithione-M* and *dithiolate-M* coordination plane varies between 4° and 8°, whereas in **2** and **3** it is 2° and 1°, respectively.



⁶⁰ **Fig. 1** Molecular structures of [Pd(Prⁱ₂pipdt)(dmit)] (**2**) (above) and of [Pt(Prⁱ₂pipdt)(dmit)] (**3**) (below) with thermal ellipsoids drawn at the 30% probability level.

Table 2 Selected bond distances (\AA) and angles ($^\circ$) for **2** and **3**

2	3
Pd-S(1)	2.2714(9)
Pd-S(2)	2.2837(8)
Pd-S(3)	2.296(1)
Pd-S(4)	2.2842(8)
C(1)-S(1)	1.685(3)
C(2)-S(2)	1.696(3)
C(11)-S(4)	1.729(3)
C(12)-S(3)	1.743(3)
C(1)-C(2)	1.489(4)
C(11)-C(12)	1.343(4)
S(1)-Pd-S(2)	87.96(3)
S(1)-Pd-S(4)	89.39(3)
S(2)-Pd-S(3)	91.48(3)
S(3)-Pd-S(4)	91.14(3)
C(1)-S(1)-Pd	106.4(1)
C(2)-S(2)-Pd	105.3(1)
C(12)-S(3)-Pd	100.21(9)
C(11)-S(4)-Pd	100.83(9)
Pt-S(1)	2.275(1)
Pt-S(2)	2.275(1)
Pt-S(3)	2.279(1)
Pt-S(4)	2.284(1)
C(1)-S(1)	1.702(5)
C(2)-S(2)	1.701(5)
C(11)-S(4)	1.713(5)
C(12)-S(3)	1.730(5)
C(1)-C(2)	1.490(6)
C(11)-C(12)	1.287(7)
S(1)-Pt-S(2)	87.74(5)
S(1)-Pt-S(4)	90.72(5)
S(2)-Pt-S(3)	90.41(4)
S(3)-Pt-S(4)	91.13(5)
C(1)-S(1)-Pt	106.5(2)
C(2)-S(2)-Pt	106.2(2)
C(12)-S(3)-Pt	99.2(2)
C(11)-S(4)-Pt	99.8(2)

The metal-sulphur bond distances are in the relatively narrow ranges of 2.2714(9)-2.296(1) \AA (**2**) and 2.275(1)-2.284(1) \AA (**3**), so that it is not possible to correlate the M-S separation with the electronic properties of the Pr^i -pipdt (dithione) and dmit (dithiolate) ligands in each complex. On the other hand, the C-S bond distances more appropriately reflect the different nature of the ligands, since in the dithione they are significantly shorter than in the dithiolate, Table 2. Moreover, the C-C bond linked to the coordinated sulphur atoms, exhibits a double bond character for the dmit and a single bond character for the Pr^i -pipdt ligands, respectively. Since the properties of a material are strongly influenced by the structural arrangements of the molecules within the crystal lattice, in the present case it is interesting to compare the crystal packing features of (**2**) and (**3**) with those exhibited by $[\text{Pd}(\text{Bz}_2\text{pipdt})(\text{dmit})]$ (**5**) and $[\text{Pt}(\text{Bz}_2\text{pipdt})(\text{dmit})]$ (**6**).^{3e} Complexes **1** and **2** are isostructural therefore their overall features can be described together (Fig.s S1 and 2). On the other hand, the crystal packing of **2** and **3** is markedly different, as can be appreciated by comparing Fig.s 2 and 3. In **2**, two complex molecules are stacked in a head-to-tail fashion and the shortest contact is exhibited by the S(7) and C(1)' atoms of two molecules (3.40 \AA , $' = -x; -y; -z$). The Pd atom is partly overlying with the peripheral C=S moiety of dmit and the methyl and one molecule ($\text{C-H}_{\text{methyl}} \cdots \text{C}(13) = 2.80 \text{ \AA}$, $\text{C-H}_{\text{methylene}} \cdots \text{S}(7) = 2.92 \text{ \AA}$). According to the presence of these interactions, the dimeric unit are arranged nearly perpendicularly to each other in the crystal packing, see Fig. 2. The crystal packing of **3** is rather different, in fact the complex molecules are partially stacked above each other by virtue of a series of interactions exchanged by the dmit ligand and the aliphatic groups of the Pr^i pipdt ligands of adjacent molecules (see Fig. 3).

These contacts lead to the formation of supramolecular layers that run parallel to the *bc* crystallographic plane and the layers exchange hydrophobic interactions by means of the Pr^i residues of the Pr^i pipdt ligand.

The substitution of the *i*-Propyl residue of Pr^i pipdt with the benzyl group in Bz_2pipdt modifies the number and types of interactions that can be exchanged by the peripheral fragments of

the ligands. In particular, the presence of the aromatic rings introduces the possibilities of $\pi \cdots \pi$ stacking as well as $\text{CH} \cdots \pi$ interactions. This in fact is evident in the crystal structure of **5** and **6**, where the molecules are arranged in a head-to-tail columnar stacking and the supramolecular interactions between the columns derives by the $\pi \cdots \pi$ stacking of the benzyl residues, Fig.s 4 and 5. The packing within each column is slightly different for **5** and **6**. In fact, in **5** the Pd atoms of one molecule are located above the chelation ring of the Bz_2pipdt with the minimum distances exhibited by the metal and the sulphur atoms ($\text{Pd} \cdots \text{S}(2)' = 3.71 \text{ \AA}$, $' = -x; -y; 1-z$; $\text{Pd} \cdots \text{S}(1)'' = 3.71 \text{ \AA}$, $'' = 1-x; -y; 1-z$). In **6**, the metal lies between two hexa-atomic rings of the Bz_2pipdt ligands with the minimum distances exhibited by the metal and the nitrogen atoms ($\text{Pt} \cdots \text{N}(2)' = 3.73 \text{ \AA}$, $' = -x; 1-y; -z$; $\text{Pt} \cdots \text{N}(1)'' = 3.73 \text{ \AA}$, $'' = 1-x; 1-y; -z$). In **6**, the metal lies between two hexa-atomic rings of the Bz_2pipdt ligands with the minimum distances exhibited by the metal and the nitrogen atoms ($\text{Pt} \cdots \text{N}(2)' = 3.73 \text{ \AA}$, $' = -x; 1-y; -z$; $\text{Pt} \cdots \text{N}(1)'' = 3.73 \text{ \AA}$, $'' =$

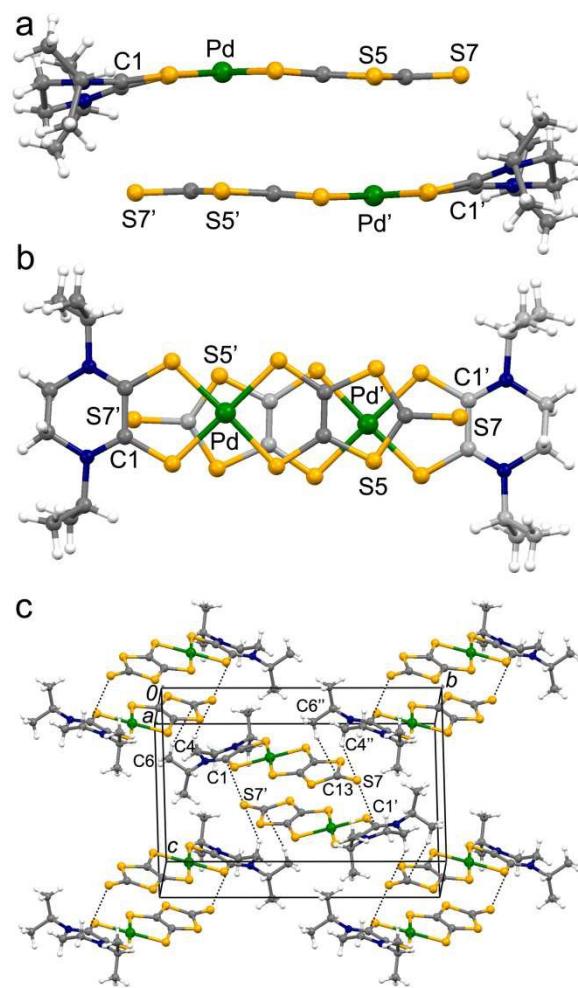


Fig. 2 Depiction of the dimer formed by two stacked $[\text{Pd}(\text{Pr}^i\text{pipdt})(\text{dmit})]$ molecules, side view (a), top view (b). Crystal packing of $[\text{Pd}(\text{Pr}^i\text{pipdt})(\text{dmit})]$ projected along the *a* axis. Dashed bonds indicates short contacts (c). Symmetry codes $' = -x; 1-y; 1-z$; $'' = 1/2-x; 1/2+y; 1/2-z$.

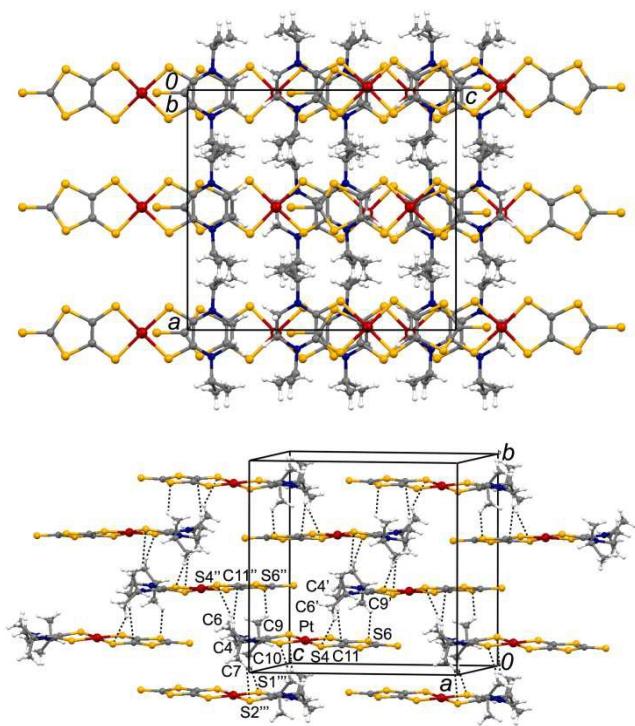


Fig. 3 Crystal packing of $[\text{Pt}(\text{Pr}_2\text{pipdt})(\text{dmit})]$ projected along the *a* axis (above) and along the *b* axis (below). Dashed bonds indicate short contacts. Symmetry codes ' = x ; $1/2-y$; $z-1/2$; " = x ; $1/2-y$; $1/2+z$, "" = $1-x$; $-y$; $2-z$.

1– x ; 1– y ; – z). Within the columnar stack, in **6** the molecules exhibit a more pronounced shift of the coordination planes with respect to **5** that together with the different orientation of the benzyl groups influences the packing modes of the two compounds: 1) in **6** the columns interact more strongly through the peripheral sulphur atoms and the CH_2 groups of the Bz_2pipdt ligands, and 2) within the stack, the benzyl residues of one molecule are interacting with the sulphur atoms involved into the metal coordination of an overlaid complex molecule. A significantly different packing is exhibited by **4** (Fig. 6), where the molecules are stacked in a head-to-head fashion with the Ni atom that is located between the CH_2 of the hexa-atomic ring and the peripheral $\text{C}=\text{S}$ residue of a Bz_2pipdt and a dmit ligands, respectively ($\text{Ni}\cdots\text{H}(2)' = 2.68 \text{ \AA}$, ' = x ; y ; $z-1$; $\text{Ni}\cdots\text{C}(2)'' = 3.67 \text{ \AA}$, '' = x ; y ; $z+1$). Moreover, the benzyl residue in **4** are oriented on the same side of the molecular plane at variance with the structure of **5** and **6** where the same groups are oriented on opposite sides. As a consequence, the interaction exchanged by the benzyl moieties in **4** and **5/6** are markedly different. The extensive net of $\pi\cdots\pi$ stacking in **5/6** is no longer present in **4**, in which adjacent columns interact through the aromatic rings and the sulphur atoms involved into the metal coordination ($\text{C}(10)''' \cdots \text{S}(1) = 2.987 \text{ \AA}$, ''' = $1-x$; $1-y$; $1-z$). Furthermore, in **4** the molecules belonging to different stacks are oriented in a V fashion with the angle between the mean molecular planes is approximately 73° .

A thorough comparison between the packing of the six complexes can be obtained by inspecting the fingerprint plots derived by the Hirshfeld surface analysis, Fig. 7. For all complexes the main types of interactions are those involving the

hydrogen and the sulphur atoms. Despite the fact that **1** and **2** are isostructural there are some differences between their fingerprint plots and this may be a consequence of the shorter coordination bond length in **1** with respect to **2**, causing some modification of the overall crystal packing between the molecules. It is also interesting to note that the interactions involving the sulphur atoms are more important for **1–3** than for **4–6**. In addition in **4–6** a significant fraction of the interactions exchanged by the molecules comprises the carbon atoms, in agreement with the presence of a significant number of $\pi\cdots\pi$ and $\text{CH}\cdots\pi$ interactions exchanged by the benzyl residues. For the sake of completeness it should be mentioned that in similar molecular systems, the use of the Fukui functions was proposed as a valuable tool for the identification of the potential sites of interactions between adjacent molecules in the solid state.^{2d}

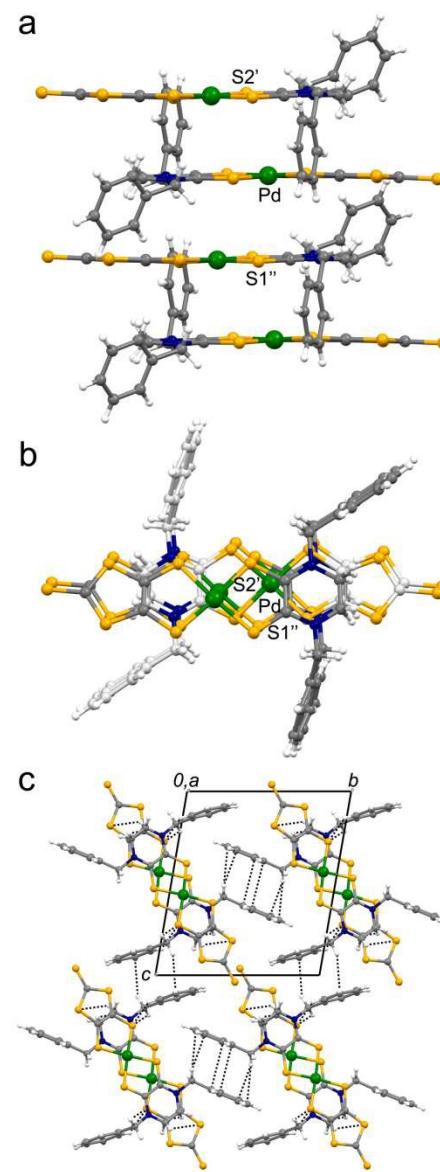


Fig. 4 Portion of the molecular stack of $[\text{Pd}(\text{Bz}_2\text{pipdt})(\text{dmit})]$, side view (a), top view (b). Symmetry codes ' = $-x$; $-y$; $1-z$. '' = $1-x$; $-y$; $1-z$. **5** Crystal packing of $[\text{Pd}(\text{Bz}_2\text{pipdt})(\text{dmit})]$ projected along the *a* axis (c).

Dashed bonds indicate short contacts. Color code: Pd, green, S, yellow, C, gray, H, white, N, blue.^{3e}

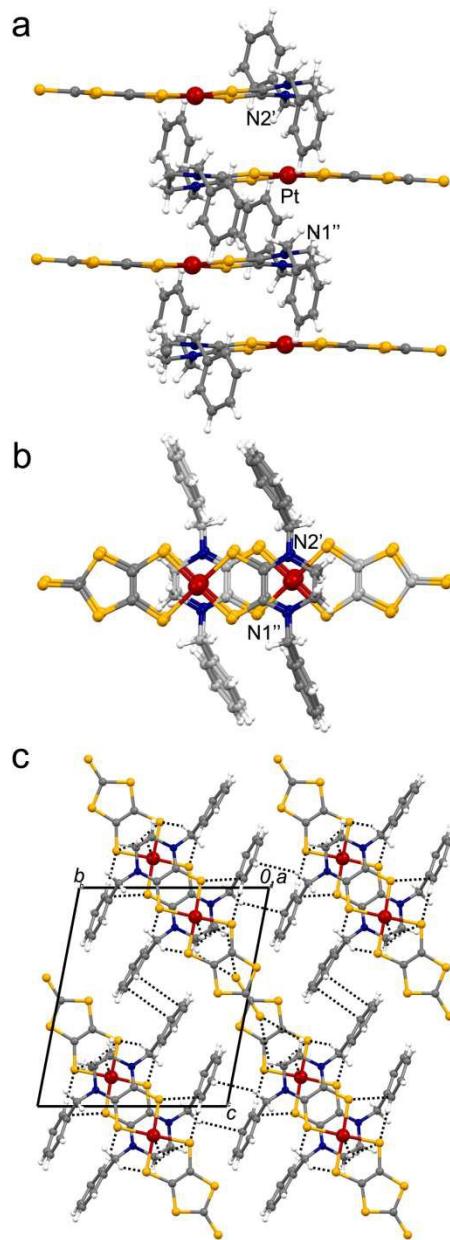


Fig. 5 Portion of the molecular stack of $[\text{Pt}(\text{Bz}_2\text{pipdt})(\text{dmit})]^{3e}$. (a), top view (b). Symmetry codes ' = $-x$; $1-y$; $-z$; '' = $1-x$; $1-y$; $-z$. Crystal packing of $[\text{Pt}(\text{Bz}_2\text{pipdt})(\text{dmit})]$ projected along the a axis (c). Dashed bonds indicate short contacts. Color code: Pt, scarlet, S, yellow, C, gray, H, white, N, blue.^{3e}

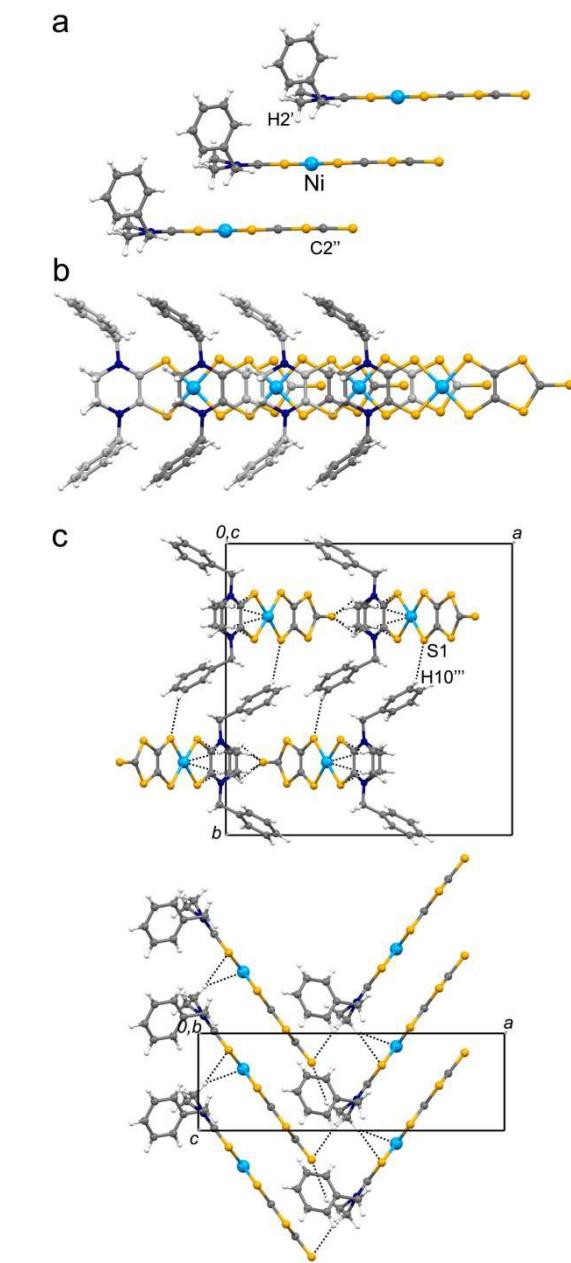


Fig. 6 Portion of the molecular stack of $[\text{Ni}(\text{Bz}_2\text{pipdt})(\text{dmit})]_6$. (a), top view (b). Crystal packing of $[\text{Ni}(\text{Bz}_2\text{pipdt})(\text{dmit})]$ projected along the c axis and along the b axis (c). Dashed bonds indicate short contacts. Color code: Ni, light blue, S, yellow, C, gray, H, white, N, blue.

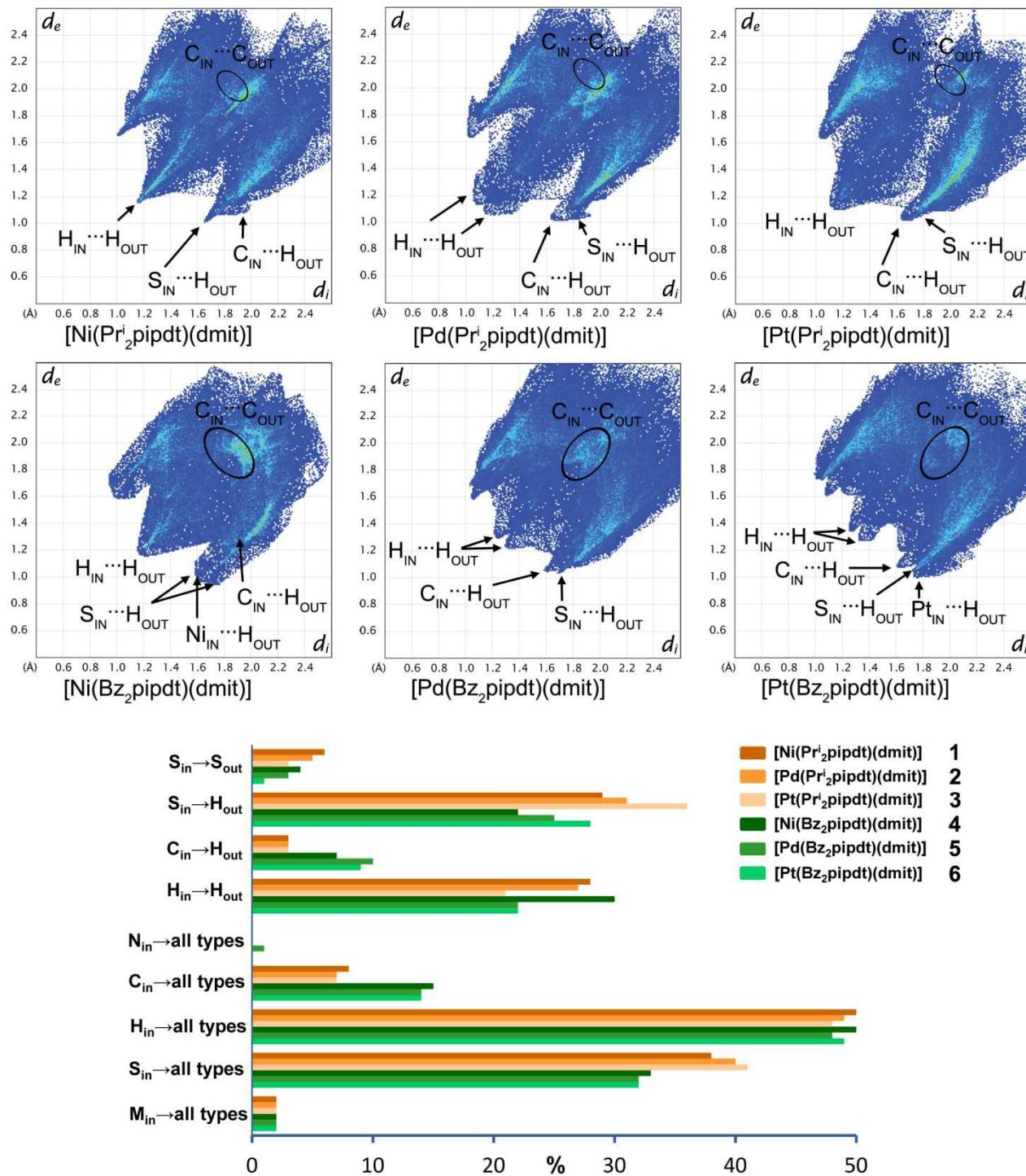


Fig. 7 Above, fingerprint plots of the complexes $[M(Bz_2pipdt)(dmit)]$ and $[M(Pr^i_2pipdt)(dmit)]$ ($M = Ni, Pd, Pt$); d_e and d_i represent the distance from the Hirshfeld surface to the nearest nucleus outside or inside, respectively, the surface. Color codes varying from blue to red highlights the frequency with which a (d_e , d_i) is observed. Below, percentage contribution of the various intermolecular contacts exchanged by $[M(Bz_2pipdt)(dmit)]$ and $[M(Pr^i_2pipdt)(dmit)]$ ($M = Ni, Pd, Pt$) with the surrounding environment reported as coloured bars as derived by the fingerprint plot analysis.

Table 3 Optical and EFISH results for **1–3**.

Complex	λ_{\max} (nm)	$\epsilon \times 10^{-3}$ (M ⁻¹ cm ⁻¹)	$\mu\beta_\lambda$ (10 ⁻⁴⁸ esu)*
[Ni(Pr ⁱ ₂ pipdt)(dmit)]	827 (707; 843)**	8.6	-6200
[Pd(Pr ⁱ ₂ pipdt)(dmit)]	775 (700; 828)**	5.5	-4700
[Pt(Pr ⁱ ₂ pipdt)(dmit)]	790 (731; 805)**	13.3	-7300

* In DMF, the uncertainty of the measure is between $\pm 10\%$.

** determined by deconvolution of the above peak

5

Visible Absorption Spectroscopy and EFISH data. Complexes **(1–3)** are characterized in the visible region by a highly negative solvatochromic band broad peak. This band is accompanied by a second one, which appears either as a shoulder in the high-energy 10 edge or just widens the main band. (Fig. S4). The wavelengths of these two components have been determined by de-convolution of the overlapping bands and are reported in Table 3. Results from time-dependent density functional theory (TD-DFT) calculations^{3b,4} suggest that the first band can be assigned to a 15 mixed metal-ligand-to-ligand charge-transfer transition (MLL'CT) and can be up to a point described as a HOMO→LUMO one, where the HOMO is formed by a mixture of metal and dithiolate orbitals while dithione orbitals give a predominant contribution to the LUMO. On the other hand, the 20 populated state has a slight multiconfigurational character, since the contribution of the latter is predominant but not unique. The shoulder at higher energy is relatable HOMO-1→LUMO transition, where the HOMO-1 is formed by a mixture of metal, dithiolate and dithione orbitals, but the very low value of the 25 oscillator strength of this transition can make this peak not observable.^{3c,4}

EFISH experiments, as described in the Experimental Section, allowed to determine the scalar product $\mu\beta_\lambda$ (μ = ground state dipole moment; β_λ = projection of the vectorial component of the 30 quadratic hyperpolarizability tensor along the dipole moment axis). The $\mu\beta_\lambda$ values determined at 1907 nm incident wavelength are listed in Table 3, and can be extrapolated to zero frequency by applying the equation: $\beta_0 = \beta_\lambda [1 - (2\lambda_{\max}/\lambda)^2] [1 - (\lambda_{\max}/\lambda)^2]$ giving for $\mu\beta_0$ (10⁻⁴⁸ esu) -1247 (-1089) **(1)**; -1332 (-938) **(2)**; -1896 35 (-1735) **(3)**. In italics the values obtained with λ_{\max} resulting for deconvolution of the broad band. Given the high approximation in their determination, the obtained values can be considered roughly comparable with those determined for **4–6** [$\mu\beta_0$ (10⁻⁴⁸ esu) -926 **(4)**; -1146 **(5)**; -1804 **(6)**] suggesting that the substitution 40 of Bz groups with Prⁱ ones in R₂pipdt does not affect significantly the second-order NLO response in the [M(R₂pipdt)(dmit)] complexes, and confirm that the largest value is found for the platinum complex. A β_0 value -130×10^{-30} esu has been determined for **1** by solvatochromic method.^{1d}

45 Notably, the $\mu\beta_0$ values of these mixed-ligand dithiolene complexes are among the highest values so far reported for metal complexes and are also high compared to those of organic

second-order NLO chromophores.¹⁹

Previous theoretical studies have shown that the remarkable first 50 molecular hyperpolarizability of metal R₂pipdt/dmit derivatives can be attributed, in addition to a high difference in dipole moments between excited and ground state and the low energy of the charge transfer transition, both to the lowest torsion angles of *dithione-M* and *dithiolate-M* coordination plane and to the π 55 system extent of its dithiolate ligand, dmit, which confirms it to behave as an optimal candidate as donor in donor-acceptor mixed-ligand dithiolene complexes to achieve high second order NLO activity. It has been shown that the order of the above cited dithione torsion angle for this class of complexes correlates 60 inversely with the oscillator strength and $\mu\beta_0$. The hyperpolarizability can be expressed as in equation 1, in terms of the simple two-state model:²⁰

$$\beta_{CT} = \frac{(\mu_e - \mu_g)\mu_{ge}^2}{\Delta E_{ge}^2} \quad (1)$$

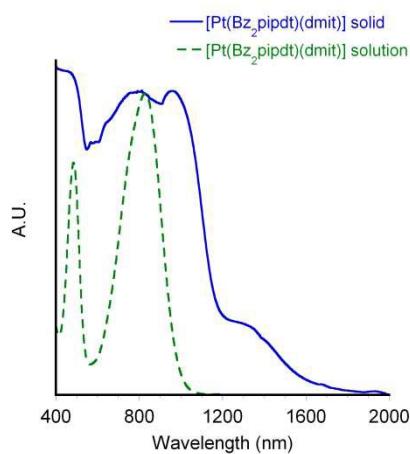
where μ_e is the excited state dipole moment, μ_g is the ground state 65 dipole moment, μ_{ge} is the transition state dipole moment and ΔE_{ge} is the transition energy between the two states. The favorable influence of the low torsion angle in Prⁱ derivatives may balance the less favourable transition energy between the two states (see 70 results from electrochemical experiments below) to achieve similar first molecular hyperpolarizabilities, as observed in corresponding metal complexes of the **1–3** and **4–6** triads.

In the solid state the bands relatable to the HOMO–LUMO transition are shifted to lower energy and a shoulder at lower energy accompanies this band, reflecting the influence of packing 75 in electronic characteristics of these solids and enlarging their absorption range in the near infrared region, as shown for **6** in Fig. 8, and for **3**, **4** and **5** in Fig.s S5, S6,. The comparison of Diffuse Reflectance Spectra of **3** and **6** is also reported in Fig. 9 and Fig. S7 for **2** and **5**. The shift to higher wavelengths of the 80 shoulder in the NIR region (approximately 1280 nm for **3** and 1340 nm for **6**) is likely due to the additional $\pi \cdots \pi$ stacking interactions observed in the Bz derivative. Spectra of **1** and **4**, are available in ref. 6, and show that no shoulder relatable to π stacking appears in **4**, in agreement with its solid state packing 85 motifs. Recently the interesting spectroscopic properties of solids based on platinum diimine-dithiolato complexes alone or acting as donors towards nitrofluorenone acceptors have been investigated.²¹ These solids, which exhibit continuous absorptions spanning from the ultraviolet to near infrared, have been termed 90 “black absorber” and are presented as materials of interest for molecule-based solar cells, given red and NIR photons constitute more than 50% of the solar radiation.²¹ The similarity of spectroscopic as well of electrochemical and structural features of d⁸ dithione-dithiolato complexes with those of diimine-dithiolato 95 ones,¹ makes these complexes promising candidates to be investigated for similar purposes.

Electrochemistry. Cyclic voltammetric experiments performed on DMF solutions of the complexes exhibit two reversible reduction waves and one irreversible oxidation wave as reported 100 in Table 4. The reduction processes occurs at slight more negative values with respect to those found for the corresponding Bz₂pipdt ligands (see CV scans in Fig. S8 as a representative

example for **3**). The reduction processes are heavily influenced by the features of the LUMO. According to the prevalent contribution of the dithione ligand to this orbital, the less negative values for the reduction processes in Bz derivatives should be ⁵relatable to their higher capability to accommodate negative charge with respect to corresponding Prⁱ ones.

The oxidation potential (E_a) is correlated to ease of one electron of metal and dithiolate orbitals. Accordingly E_a should depend both on the metal and the dmit, and thus comparable E_a values are



20 Fig. 8 Comparison of Solid state Diffuse Reflectance (continuous line) and DFM solution spectra (dashed line) of **6** in arbitrary units.

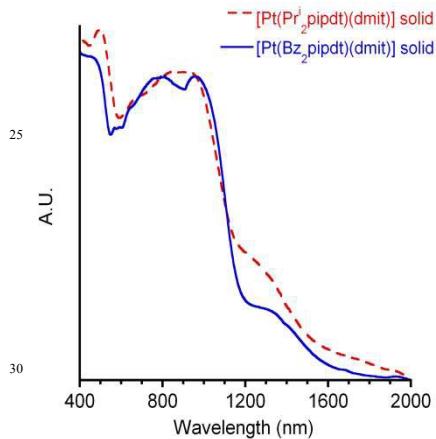


Fig. 9 Comparison of Diffuse Reflectance spectra of **3** (continuous line) and of **6** (dashed line).

35 Table 4 Cyclic voltammetric data. Measured at the Pt electrode in DMF, 0.1 M Bu₄NBF₄ (reference electrode Ag/AgCl) for **1-3**. Corresponding data for **4-6** are reported for comparison (ref 3e).

Complex	E_a (V) ^a	$E^{1/2}$ (V)	$E^{2/2}$ (V)
0→+1	0→-1	-1→-2	
[Ni(Pr ⁱ 2pipdt)(dmit)]	+1.01	-0.49	-1.04
[Pd(Pr ⁱ 2pipdt)(dmit)]	+0.84	-0.38	-0.93
[Pt(Pr ⁱ 2pipdt)(dmit)]	+0.71	-0.42	-0.96
[Ni(Bz₂pipdt)(dmit)]	+0.69	-0.41	-0.91
[Pd(Bz ₂ pipdt)(dmit)]	+0.84	-0.36	-0.81
[Pt(Bz ₂ pipdt)(dmit)]	+0.86	-0.39	-0.84

^a Irreversible.

¹⁰ predictable for complexes having the same metal among the series. This happens for the Pd case only. However it must be removal process from the HOMO, which is formed by a mixture remarked that the reason of the irreversibility of the oxidation ¹⁵process is not clear and may be related to the formation of insoluble or decomposition products. Thus the possible deposition of the oxidized species as a film on the electrode surface may alter the measured E_a values, hindering their reliability.

Conclusions

²⁰ The [M(R₂pipdt)(dmit)] Ni-Pt triads based on donor/acceptor S,S' ligands were investigated in order to assess the role of the functionalization of the pipdt ligand on the properties of the complexes. When substituting the isopropyl for the benzyl groups in the piperazine-2,3-dithione ligand, only minor changes are ²⁵induced in their properties in solution, given their very similar molecular structures. Both **1-3** and **4-6** triads behave as redox active second-order NLO chromophores and exhibit comparable high negative molecular quadratic optical non linearity. Moreover studies on ultrafast excited-state dynamics of these complexes, ³⁰investigated by transient absorption spectroscopy on the femtosecond-picosecond timescale, show a common photo-behavior for the two triads, although individual kinetics parameters and quantum yields can vary with the metal, the dithione ligand and the solvent.²² On the other hand, different ³⁵structural features are observed in their crystal packing upon changing R from Bz to Prⁱ in the piperazine ring, and also, more surprisingly, inside the triads when changing the metal ion. In **1** and **2**, two complex molecules are stacked in a head-to-tail fashion forming a dimeric entity, whereas in **3** the complex ⁴⁰molecules are partially stacked above each other leading to the formation of supramolecular layers. The presence of the aromatic rings of Bz in **4-6** introduces the possibility of additional interactions in the solid state such as $\pi\cdots\pi$ stacking and CH $\cdots\pi$ interactions. Moreover, the conformational flexibility of the ⁴⁵benzyl residue gives rise to different arrangements of the benzyl residues of pipdt with respect to the molecular plane. The benzyl groups may be oriented on the same side, as in **4**, or on opposite side, as in **5/6**. These additional degrees of freedom is not present in **1-3**, where the i-propyl residues adopt a unique conformation ⁵⁰that minimizes the steric hindrance between the methyl groups and the molecular plane. According to the Hirshfeld surface analysis a good portion of the interactions exchanged by the complexes are those occurring between the hydrogen atoms with the surrounding molecules, followed by the interactions ⁵⁵exchanged by the sulphur atoms. The third main type of interaction is that involving the carbon atoms. There is however a distinctive pattern that differentiate **1-3** from **4-6**. In particular, the interactions involving the sulphur atoms are more important for **1-3** than for **4-6**, while a significant fraction of the ⁶⁰interactions comprises the carbon atoms in **4-6**. This is in agreement with the presence of a significant number of $\pi\cdots\pi$ and CH $\cdots\pi$ interactions exchanged by the benzyl residues. Intermolecular interactions shift to higher wavelengths the ⁶⁵absorbance range of these solids, which spans from the ultraviolet to the near infrared region, making these compounds of interest as redox active "black" absorbers.

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† Electronic Supplementary Information (ESI) available: Fig. S1. Structural features of [Ni(Pr₂pipdt)(dmit)]; Fig. S2. Vis/NIR absorption spectra and solvatochromic behaviour of [Ni(Pr₂pipdt)(dmit)]; Fig. S3 Vis/NIR absorption spectra and solvatochromic behaviour of [Pd(Pr₂pipdt)(dmit)]; Electrochemical measurements of [Pt(Bz₂pipdt)(dmit)]; Fig. S4 Hirshfeld surface for the three complexes [M(Pr₂pipdt)(dmit)] (M = Ni, Pd, Pt); Fig. S5 Hirshfeld surface for the three complexes [M(Pr₂pipdt)(dmit)] (M = Ni, Pd, Pt)]. See DOI: 10.1039/b000000/x/

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Structural changes in M^{II} dithione/dithiolato complexes (M = Ni, Pd, Pt) on varying the dithione functionalization

Large differences in the crystal structures of the title triads, induced by diverse number and types of interactions exchanged by the peripheral fragments of the ligands, have been found and described in detail through the Hirshfeld surface analysis. These interactions shift to the NIR the absorbance range of these chromophores in the solids.

