ABSTRACT: The reaction of the bis(1,2-dithiolene) complex [Pd-(Me₂timdt)₂] (1; Me₂timdt⁺⁺ = monoreduced 1,3-dimethyl-2,4,5-trithioxoimidazolidine) with Br₂ yielded the complex [Pd(Me₂timdt)Br₂] (2), which was reacted with Na₂mnt (mnt⁻⁻ = 1,2-dicyano-1,2-ethylenedithiolate) to give the neutral mixed-ligand complex [Pd(Me₂timdt)(mnt)] (3). Complex 3 shows an intense solvatochromic near-infrared (NIR) absorption band falling between 955 nm in DMF and 1060 nm in CHCl₃ (ε = 10700 M⁻¹ cm⁻¹ in CHCl₃). DFT calculations were used to elucidate the electronic structure of complex 3 and to compare it with those of the corresponding homoleptic complexes 1 and [Pd(mnt)₂] (4). An in-depth comparison of calculated and experimental structural and vis–NIR spectroscopic properties, supported by IEF-PCM TD-DFT and NBO calculations, clearly points to a description of 3 as a dithione-dithiolato complex. For the first time, a broken-symmetry (BS) procedure for the evaluation of the singlet diradical character (DC) of heteroleptic bis(1,2-dithiolene) complexes has been developed and applied to complex 3. The DC, predominant for 1 (n_DC = 55.4%), provides a remarkable contribution to the electronic structures of the ground states of both 3 and 4, showing a diradicaloid nature (n_DC = 24.9% and 27.5%, respectively). The computational approach developed here clearly shows that a rational design of the DC of bis(1,2-dithiolene) metal complexes, and hence their linear and nonlinear optical properties, can be achieved by a proper choice of the 1,2-dithiolene ligands based on their electronic structure.

INTRODUCTION

The interest of the scientific community toward bis(1,2-dithiolene) metal complexes has been continuously increasing during the past few decades, accompanied by a growing number of applications relying on the superconducting, photoconducting, magnetic, and linear and nonlinear optical properties of this class of compounds. Bis(1,2-dithiolene) complexes [M(R₂C₂S₂)₂]⁻ of d⁸ metal ions M⁺⁺ such as Ni⁺⁺, Pd⁺⁺, Pt⁺⁺, and Au⁺⁺, feature peculiar properties, such as molecular planarity and the ability to exist in well-defined oxidation states typically ranging between x = 4 and x = 2, also assuming fractional charges in nonintegral oxidation state (NIOS) salts. The redox noninnocence of the 1,2-dithiolene ligands (Scheme 1) renders it difficult to partition the charge of the complexes between the ligands L and the central metal ion M⁺⁺.

The typical redox steps accessible to bis(1,2-dithiolene) complexes of group 10 metals (M = Ni, Pd, Pt) are summarized in Scheme 2. Dianionic bis(1,2-dithiolene) complexes [ML₂]⁻⁻ are diamagnetic species, which can be...
Scheme 2. Differently Charged Species and Resonance Forms of Bis(1,2-dithiolene) Metal Complexes (M = Ni, Pd, Pt; q = 0, 1, 2)

isolated as stable anions in salts such as \((\text{Ph}_3\text{P})_2[\text{Ni}(\text{mnt})_2]\) (mnt\(^2\) = maleonitrile-1,2-dithiolate, 1,2-dicyano-1,2-ethylidenedithiolate).\(^{39}\) These species are fully described as \([\text{M}^{\text{II}}(\text{L}^2\text{−})]^\text{−}\) complexes, featuring the ene-1,2-dithiolato form L\(^2\)− of the ligands (d in Scheme 1). Paramagnetic monoanionic 1,2-dithiolene complexes [ML\(_2\)]\(^{−}\) can be represented as \([\text{M}^{\text{II}}(\text{L}^2\text{−})]^\text{−}\) compounds \(^{10,33}\) or by two resonance forms showing the dianionic ligand L\(^2\)− (d in Scheme 1) and a monoanionic radical ligand L\(^{−}\)• (c in Scheme 1); i.e., \([\text{M}^{\text{II}}(\text{L}^2\text{−})](\text{L}^{−})^\text{−}\)\(^{27}\). In diamagnetic neutral complexes [ML\(_2\)], the central metal ion can carry formal charges varying between 0 and +4, while the ligands can assume a neutral, monoanionic, or dianionic charge (Scheme 2), indicating a large degree of \(\pi\)-electron delocalization involving the metal as well as the L ligands (metalloaromaticity).\(^{32}\) Spectroscopic and theoretical results suggest that the complexes are better described as formed by the metal dication M\(^{\text{II}}\), whatever the charge on the complex.\(^{27,33}\) Therefore, the oxidation/reduction steps leading from [ML\(_2\)]\(^2\)− to [ML\(_2\)]\(^{−}\) are mainly located on the ligands;\(^{10,33}\) analogously to what has been reported for \([\text{Au}^{\text{III}}(\text{Ar-edt})_{2}]^{−}\)\(^{30}\) complexes (Ar-edt\(^{2−}\) = arylethylene-1,2-dithiolate; Ar = phenyl, 2-naphthyl, 2-pyrenyl).\(^{36}\) Hence, the neutral M\(^{\text{II}}\) complexes can be described as dianionic singlet species formed by two antiferromagnetically coupled monoanionic radical ligands, \([\text{M}^{\text{II}}(\text{L}^{−})]^\text{−}\);\(^{33,37}\) Indeed, neither the closed-shell (CS) restricted delocalized nor the localized singlet diradical description represents reliably the ground state (GS) of neutral bis(1,2-dithiolene) complexes, so that an index \(n_{\text{DC}}\) of the diradical character (DC) can be calculated to evaluate the relative weight of the diradical singlet description.\(^{37−39}\) Notably, different optical properties in the visible/near-infrared (vis/NIR) region are associated with the differently charged forms of bis(1,2-dithiolene) complexes (electrochromism).\(^{16,40,53}\) Neutral complexes [ML\(_2\)] show a peculiar intense absorption in the region above 800 nm,\(^{2,3,30}\) This band, attributed to a \(\pi−\pi^*\) HOMO \(\rightarrow\) LUMO (H \(\rightarrow\) L) one-electron excitation,\(^{5,6}\) is shifted to lower energies and lowered in intensity in the corresponding monoreduced forms [ML\(_2\)]\(^{−}\);\(^{41}\) while the dianions [ML\(_2\)]\(^2\)− do not show any vis/NIR absorption. In this context, for a few decades, some authors have been investigating the \([\text{M}(\text{R}_2\text{timdt})]^{2+}\) class of photoconducting \(^{42−44}\) complexes (R\(_2\text{timdt}\) = monoreduced 1,3-disubstituted imidazoline-2,4,5-trithione; M = Ni, Pd, Pt; \(q = 0, 1, 2; \text{Chart S1}\));\(^{55−58}\) Neutral \([\text{M}(\text{R}_2\text{timdt})]_{2}\) complexes show a strikingly intense absorption at about 1000 nm (molar extinction coefficient \(\epsilon\) as large as 120000 M\(^{−1}\) cm\(^{−1}\) in toluene),\(^{48}\) whose energy can be fine-tuned by a proper choice of the metal M and the substituents R\(_q\).\(^{46,48}\) The corresponding reduced forms show a NIR absorption falling at about 1450 nm for M = Ni, Pt and at about 1700 nm for M = Pd.\(^{51}\)

Mixed-ligand bis(1,2-dithiolene) complexes \([\text{M}(\text{L})(\text{L}′)]\) have been much less investigated than homoleptic complexes,\(^{48,53}\) and are often prepared by metathesis reactions.\(^{34−56}\) The synthetic way of obtaining \([\text{M}(\text{L})(\text{L}′)]\) complexes by replacement of halides in ML\(_2\) complexes has been previously reported in a few cases.\(^{48}\) In these complexes, most often containing a Ni\(^{\text{II}}\) ion, the electron withdrawing “pull” ligand L tends to assume the ene-1,2-dithiolate form L\(^2\)− (d in Scheme 1), with shorter C−C and longer C−S bond distances, while the other “push” ligand L′ assumes a 1,2-dithione form (b in Scheme 1), with longer C−C and shorter C−S distances, so that the complex is generally described as the dithione-dithiolato species \([\text{M}^{\text{II}}(\text{L}^{2−})(\text{L}′)]\);\(^\text{[45]}\) The electronic structure of these complexes in their neutral state, reminiscent of that of diimine-dichalconogenolate complexes,\(^{62−64}\) shows the HOMO featuring a larger contribution from the “pull” ligand L\(^2\)− and the LUMO from the “push” ligand L′. The peculiar visible/near-IR (vis/NIR) electron transition of the neutral species assumes a partial charge-transfer (CT) character from the 1,2-dithiolato L\(^2\)− ligand to the 1,2-dithione L′ (L′CT), testified by a remarkable negative solvatochromism of the resulting absorption band.\(^{54}\) In comparison to homoleptic complexes, the DC of heteroleptic bis(1,2-dithiolene) complexes has not been investigated, implicitly accepting that the GS configuration of these complexes is fully defined by the dithione-dithiolato CS description.\(^{48}\) Nevertheless, it is conceivable that a continuous variation from ideally pure open-shell singlet diradicals \([\text{M}^{\text{II}}(\text{L}^2\text{−})](\text{L}^{−})^\text{−}\) to CS dithione-dithiolato complexes \([\text{M}^{\text{II}}(\text{L})](\text{L}^{−})^\text{−}\) occurs as the difference in the donor properties of the L and L′ ligands increases. Therefore, we have considered as a case study the mixed-ligand 1,2-dithiolene Pd\(^{\text{II}}\) complex featuring the well-known mnt “pull” ligand coupled to the “push” ligand Me-timdt. Herein, we report an experimental and theoretical investigation on the resulting complex [Pd(Me-timdt)(mnt)], in comparison with the relevant parent complexes [Pd(Me-timdt)]\(^2\) and [Pd-(mnt)], aimed at evaluating the role of the electronic structure of the ligands in tailoring the DC in homoleptic and heteroleptic bis(1,2-dithiolene) palladium complexes.

### Experimental Section

**Materials and Methods.** Reagents were purchased from Honeywell, Alfa Aesar, and Sigma-Aldrich and used without further purification. Solvents (reagent grade) were purchased from Honeywell, VWR, and Merck and dried by using standard techniques when required. Manipulations were performed using standard Schlenk techniques under a dry dinitrogen atmosphere. Elemental analyses were performed with a CHNS/O PE 2400 series II CHNS/O elemental analyzer (T = 925 °C). FT-IR spectra were recorded with a Thermo-Nicolet 5700 spectrometer at room temperature: KBr pellets with a KBr beam splitter and KBr windows (4000–400 cm\(^{−1}\), resolution 4 cm\(^{−1}\)) were used. Absorption spectra were recorded at 25°C in a quartz cell of 10.00 mm optical path with either a Thermo Evolution 300 (190–1100 nm) spectrophotometer or an Agilent Cary 5000 UV–vis–NIR (190–2000 nm) dual-beam spectrophotometer. Absorption spectra were decomposed into their constituent Gaussian peaks using the Specpeak 2.0\(^{65}\) and Fitxy 1.3\(^{66}\) programs. The Crystallographic Structural Database was accessed by using CCDC ConQuest 2020.1.\(^{57}\)
X-ray Diffraction Measurements. Single-crystal X-ray diffraction data were collected with a Rigaku MM007/Mercury diffractometer with Mo Kα radiation. The structure was solved by direct methods with SHELXS-97\textsuperscript{85} and refined on F\textsuperscript{2} by using SHELXL-97\textsuperscript{86}.

Synthesis. 1,3-Dimethyl-2-thiooximidozadoline-4,5-dione and a complex were prepared according to a previously reported procedure (yield 86\%\textsuperscript{45,46,70}).

Synthesis of [Pd(Me\textsubscript{2}timdt)\textsubscript{2}Br\textsubscript{2}] (2). [Pd(Me\textsubscript{2}timdt)]\textsubscript{0} (1; 35.4 mg; 7.27 × 10\textsuperscript{-2} mmol) was reacted with an excess of molecular dibromine in an Aldrich pressure tube using 30 mL of a CHCl\textsubscript{3}/CH\textsubscript{3}CN (2/1) solvent mixture. The glass vessel was heated to 130 °C for 15 min and slowly cooled to room temperature. The precipitate was filtered and washed with petroleum ether (brown solid; yield 32.1 mg, 97\%). Mp: >230 °C. FT-IR (4000–400 cm\textsuperscript{-1}): ε = 1477 (s), 1399 (s), 1360 (m), 1345 (m), 1291 (s), 1080 (s), 1032 (mw), 548 cm\textsuperscript{-1} (w). Anal. Calcld for C\textsubscript{15}H\textsubscript{14}Br\textsubscript{2}N\textsubscript{2}PdS\textsubscript{3}: C, 14.10; H, 0.76; N, 8.11. Found: C, 14.86; H, 0.33; N, 9.02.

Synthesis of [Pd(Me\textsubscript{2}timdt)(mnt)] (3). Complex 2 (30.2 mg; 6.61 × 10\textsuperscript{-2} mmol) and a molar excess of sodium 1,2-dicyanoethylene-1,2-dithiolate (21.5 mg; 0.115 mmol) were suspended in CH\textsubscript{3}CN (30 mL) in an Aldrich pressure tube. The mixture was heated to 130 °C for 30 min and slowly cooled to room temperature. The product was isolated as black needles by filtration, washed with water, and dried under vacuum (yield 8.3 mg, 29\%). Mp: >230 °C. FT-IR (4000–400 cm\textsuperscript{-1}): ε = 2925 (w), 2204 (m), 1459 (m), 1397 (ms), 1285 (s), 1150 (m), 1079 (ms), 864 (m), 551 (mw), 500 cm\textsuperscript{-1} (w). Anal. Calcld for C\textsubscript{17}H\textsubscript{16}Br\textsubscript{2}N\textsubscript{2}PdS\textsubscript{3}: C, 14.07; H, 0.76; N, 13.07.

The effective electron exchange integrals J\textsubscript{ab}\textsuperscript{83} were calculated as follows:

\[
\Delta \epsilon_{SC}^{\text{MS}} = \Delta \epsilon_{ST} = (S_{T}^{2}S_{T}^{2} - (S_{BS}^{2})_{T}^{2})
\]

Therefore, the \(\Delta \epsilon_{SC}^{\text{MS}}\) value was obtained:

\[
\epsilon_{SC}^{\text{MS}} = \epsilon_{T} + \Delta \epsilon_{ST} = (S_{T}^{2}S_{T}^{2} - (S_{BS}^{2})_{T}^{2})
\]

The diradical character index \(n_{DC}\) can be directly calculated from (S\textsuperscript{2}BS)\textsuperscript{17,37}

\[
n_{DC} = 1 - \sqrt{1 - (S_{BS}^{2})_{T}^{2}}
\]

A complete natural population analysis (NPA) was carried out with a natural bonding orbital (NBO)\textsuperscript{88} partitioning scheme (\(\text{pop} = \text{br} + \text{orb}\)), with \(\text{basisA}\) and \(\text{basisB}\) keywords in the NBO section of the input file.) in order to investigate the charge distributions and Wiberg bond indices.\textsuperscript{97} Absorption vertical transition energies and oscillator strengths were calculated at the time-dependent (TD) DFT level.\textsuperscript{89,99} TD-DFT calculations were carried out at the optimized geometry in the gas phase and in a selection of solvents (CHCl\textsubscript{3}, DMF, THF, acetonitrile), implicitly taken into account by the computational full width at half maximum (FWHM) values of the NIR oscillator strength values calculated at the TD-DFT level along with experimental full width at half maximum (FWHM) values of the NIR band were used to evaluate the molar extinction coefficients \(\epsilon\).\textsuperscript{100} Experimental FWHM values on an energy scale (eV) were evaluated from the corresponding values \(w\) determined in nm from the experimental NIR spectra:

\[
W = 10^{7} \frac{w^{2}}{n^{2} + \frac{w^{2}}{4}}
\]

The one-photon absorption oscillator strength \(f_{\text{on}}\) for each transition \(0 \rightarrow n\) is\textsuperscript{102}

\[
f_{\text{on}} = \frac{8\pi^{2}m_{e}c_{0}^{2} |\psi_{0}|^{2}}{3c^{2}h}
\]

where \(m_{e}\) and \(\epsilon\) are the mass and the charge of the electron, \(\nu_{0}\) is the frequency (s\textsuperscript{-1}) of the transition between the states 0 and \(n\), \(\mu_{0}\) is the transition dipole moment, and \(h\) is Planck’s constant. \(f_{\text{on}}\) is related to the experimental intensity of each absorption band:
\[ f_{\text{abs}} = 4.32 \times 10^{-9} \int e(\sigma) \, d\sigma \]

where \( e \) is the molar extinction coefficient (M\(^{-1}\) cm\(^{-1}\)) and \( \sigma \) is the frequency (cm\(^{-1}\)). By adoption of Gaussian shape curves for the absorption bands

\[ f_{\text{abs}} = 4.32 \times 10^{-9} e^{-(\Delta \sigma/\sigma_0)^2} \]

\[ f_{\text{abs}} = 4.32 \times 10^{-9} \sqrt{\pi} \theta \]

where the width parameter \( \theta \) is related to \( W \) by

\[ \theta = \frac{W}{2\sqrt{\ln 2}} \]

Therefore, the equation

\[ e_{\text{calc}} = \frac{2\sqrt{\ln 2}}{4.32 \times 10^{-9} \sqrt{\pi} W} \]

allows evaluating the molar extinction coefficients of the NIR transition at the TD-DFT level. Calculated molar extinction coefficients were scaled on experimental available data to give a corrected \( e_{\text{calc}} \) value.

The nature of the minima of each structure optimized at the DFT and DFT-BS levels was verified by harmonic frequency calculations (freq = raman), including the determination of thermochromism parameters (zero-point energy (ZPE) corrections and thermal corrections to enthalpy and Gibbs free energy) and the calculation of FT-Raman frequencies. Gibbs free energies were used to calculate absolute reduction potentials at 298 K (\( E_{\text{G0}} \)) according to the following equation:

\[ E_{\text{G0}} = \Delta G_{\text{F}} \left( \frac{298}{298} \right) = \frac{\Delta G_{\text{F}}^{\text{neutron}} - \Delta G_{\text{F}}^{\text{neutral}} - \Delta G_{\text{F}}^{\text{calc}}}{F} \]

where \( \Delta G_{\text{F}}^{\text{neutron}} \) and \( \Delta G_{\text{F}}^{\text{neutral}} \) are the free energy values calculated at 298 K and \( \Delta G_{\text{F}}^{\text{calc}} \) represents the potential of the free electron (\(-0.03766 \) eV at 298 K; \( \Delta G_{\text{F}}^{\text{calc}} \) is calculated on the most stable neutral form). \( E_{\text{G0}} \) values were also referenced to the Fc+/Fc couple, taken into account at the same level of theory.

The total static (i.e., zero frequency) second-order (quadratic) hyperpolarizability (the first hyperpolarizability) \( \beta_{\text{tot}} \) was calculated as previously described.

Throughout all this work, molecules in their optimized standard orientation were rotated in order to align the main symmetry axis and DFT-BS levels was verified.

**RESULTS AND DISCUSSION**

**Synthesis.** The synthesis of [Pd(R’timdt)\(_2\)] neutral complexes can be achieved by direct sulfuration with Lawesson’s reagent (2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiodiphenylsulfide-2,4-disulfide) in dichloromethane.

The reaction of a suspension of [Pd(Me\(_2\)timdt)\(_2\)] (1) in a 2/1 CHCl\(_3\)/CH\(_3\)CN solvent mixture with a molar excess of molecular dibromine in a high-pressure tube at 130 °C yielded the neutral complex [Pd(Me\(_2\)timdt)Br\(_2\)] (2; reaction iii in Scheme 3), which was successively made to react with sodium 1,2-dicyanoethylene-1,2-dithiolate (NaN\(_2\)mnt) in CHCl\(_3\) at 130 °C to give the mixed-ligand neutral complex [Pd(Me\(_2\)timdt)-(mnt)] (3; reaction iv in Scheme 3).

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**Figure 1.** ORTEP view of complex 3 with the adopted labeling scheme. Selected bond distances (\( \AA \)) and angles (deg): Pd–S(1) 2.314(2), C(1)–S(1) 1.660(8), C(1)–C(1) 1.454(16), C(1)–N(1) 1.342(9), N(1)–C(3) 1.454(10), N(1)–C(2) 1.401(10), C(2)–S(2) 1.603(13), Pd–S(4) 2.258(2), C(4)–S(4) 1.724(8), C(4)–C(4) 1.139(10), A(1)–S–Pd–S(1) 90.61(12), S(1)–Pd–S(4) 88.92(8), C(1)–S(1)–Pd–S(4) 179.6(2), S(1)–Pd–S(4)–C(4) 177.3(2). Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry operation: (i) \( x, 1/2 + y, z \).

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**Scheme 3. Reaction Pathways for the Synthesis of 3**

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**X-ray Diffraction Studies.** Tiny needle crystals of 3, suitable for a structural characterization by X-ray diffraction analysis (Figure 1, Tables S1–S6, and Figures S1 and S2), were isolated from the reaction mixture. The structural features of 3 (Figure 1) closely resemble those determined previously for [Pd(Et\(_2\)timdt)(mnt)]. The molecule is planar except for the methyl substituents, with the central Pd ion coordinated by the Et\(_2\)timdt ligands in [Pd(Et\(_2\)timdt)\(_2\)]. When the two C\(_2\)S\(_2\)Pd bonds and passing through the central metal ion with the z axis and lie on the xy plane. Molden 6.2\(^{111}\) and Gaussum 6.0.14\(^{112}\) were used to analyze Kohn–Sham (KS) molecular orbital (MO) compositions and energies. Gaussian 3.0\(^{111}\) and Chemissian 4.54\(^{111}\) were used to evaluate the atomic orbital contributions to KS-MOs and to analyze TD-DFT data.

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The C–C distance in the Me2timdt ligand of 3 (1.454(16) Å) is intermediate between the corresponding distance in [Pd(Et2timdt)Br2] (1.474(10) Å; Chart S2),48 featuring an neutral Et2timdt ligand, and that of Li(S, R′ = 2,6-disopropylphenyl, Chart S2; 1.417(4) Å), featuring the R′-timdt™ radical monoanion.27,72 Analogously, the C(4)−C(4) distance in 3 (1.364(16) Å) is shorter than that found in [Pd(mnt)2] (4; 1.392(2) Å; Chart S2)116 and the average value for 4™ monoanions (1.377(24) Å)117 but slightly larger than the average value found in salts of the complex 4™ (1.359(19) Å).118 This suggests that the Me2timdt ligand in 3 should be considered to carry a partial negative charge and that the GS of 3 should include a partial DC. The unit cell contains pairs (Z = 2) of symmetry-related complex molecules, each forming slipped stacks along the a vector (Figures S1 and S2 in the Supporting Information) with an interplanar distance of 3.619 Å, very close to that featured by the stacks found in the crystal structure of [Pd(Et2timdt)2] (3.6 Å).45 Along the stacks, the terminal thione groups of the slightly larger than the average value found in salts of the ligand of [Pd(Et2timdt)Br2] (1.474(10) Å; Chart S2),48 the average value for 4™ monoanions (1.377(24) Å)117 but slightly larger than the average value found in salts of the complex 4™ (1.359(19) Å).118 This suggests that the Me2timdt ligand in 3 should be considered to carry a partial negative charge and that the GS of 3 should include a partial DC. The unit cell contains pairs (Z = 2) of symmetry-related complex molecules, each forming slipped stacks along the a vector (Figures S1 and S2 in the Supporting Information) with an interplanar distance of 3.619 Å, very close to that featured by the stacks found in the crystal structure of [Pd(Et2timdt)2] (3.6 Å).45 Along the stacks, the terminal thione groups of the Me2timdt ligands weakly interact with the π-system of the imidazoline ring (C(1)−C(6)−S(2) 3.420 Å; (ii) 1 − x, y, z; (iii) 1 + x, 1/2 − y, z; Figure S1). Weak contacts between the methyl substituents at the Me2timdt ligands and the terminal N atoms of the mnt ligands (H(3A)···N(S)w 2.644 Å; (iv) −1 + x, y, 1 + z) are responsible for the interactions between adjacent stacks aligned along the c direction. Notably, the crystal packing is essentially different from that found in [Pd(Et2timdt)(mnt)] (where the complex molecules are stacked in an alternate head-to-tail disposition, allowing for shorter interplanar distances (3.570 Å).48

Absorption Spectroscopy. Neutral [Pd(R′′-timdt)2] bis-(1,2-dithiolene) complexes featuring alkyl R substituents show a peculiar, intense NIR absorption falling at about 1010 nm, with molar extinction coefficients ε as high as 70000 M−1 cm−1 in CH2Cl2.45,46 The UV−vis−NIR absorption spectrum of a CH2Cl2 solution of 1 shows a NIR absorption maximum falling at 1008 nm (full width at half-maximum (FWHM) ω = 131 nm; Figure S3). Notably, the NIR peak appears at least three Gaussian components (λ1 = 1004.8 nm, ω1 = 121.9 nm, integral ratio 74.5%; λ2 = 890.3 nm, ω2 = 93.5 nm, 6.6%; λ3 = 1120.2 nm, ω3 = 155.4 nm, 18.9%; Figure S3),65 in agreement with the spectral decomposition reported for [Pd-(2,4-Bu2C6H4S)]2, for which a series of d−d transitions with different spin couplings to the open-shell ligands were envisaged.38 Complex 3 shows a well-defined intense NIR peak at 1060 nm in CHCl3 (ε = 10700 M−1 cm−1; Figure 2), in perfect agreement with the spectral features shown by [Pd(Et2timdt)(mnt)] in the same solvent (λmax = 1061 nm, ε = 12500 M−1 cm−1).48 The NIR band can be decomposed into two main peaks, each accounting for about half the area of the band (λ1 = 1066.2 nm, ω1 = 140.6 nm, 51.6%; λ2 = 1025.1 nm, ω2 = 249.5 nm, 48.4% in CHCl3; Figures S4 and S5). The NIR band displays a remarkable negative solvatochromism, with absorption maxima wavelengths ranging between 955 nm in DMF and 1060 nm in CHCl3 (Table 1). When the solvent polarity is increased, the change in the experimental spectral shapes (Figure S6) suggests that the relative weight and the energy difference between the red component and the main peak of the solvatochromic NIR band increases, so that a greater polar nature should be attributed to the higher energy peak as compared to the main peak.

Theoretical Calculations. During the past few decades, DFT calculations have been used successfully to investigate the structural features and the redox and spectroscopic properties of homoleptic and heteroleptic complexes containing 1,2-dithiolene ligands.36−39,48,50,52,62,64,72 DFT calculations were applied here on Me2timdt™, mnt™ (q = 0, 1, 2), and related compounds and the relevant neutral, monoanionic, and dianionic homoleptic and heteroleptic Pd complexes.

Ligands. The relative stability of the variously charged forms of 1,2-dithiolene ligands (Scheme 1) depends on the nature of the R substituents. The mnt ligand is generally encountered in its 1,2-dithiolate form, and the corresponding neutral species is unreported. In fact, neutral 1,2-dithiolene species are generally unstable,6 but depending on the R substituents they can be found as either 1,2-dithiones (Scheme 1, b), for instance embedded in 1,2-dithioxamides,72 or stabilized as 1,2-dithietes (Scheme 1, a),120−122 Since vicinal dithioxamides in five-membered rings are reportedly unstable,123 R′′-timdt ligands cannot be isolated as neutral 2,4,5-trithiones and the sulfauration of disubstituted 2-thioxomida-lone-4,5-diones leads to tetrasubstituted 4,5,6,7-tetrahydro-1,2-b:3,4-b′-dimidazo[2,9-d]thiophene or 4,5,9,10-tetrahydro-[1,2-b:5,6-b′]-2,7-dithione (a and b in Chart S4 in the Supporting Information, respectively), the latter type of compounds being the final product of the Br2 oxidation of [Pd(R’′-timdt)2] complexes (R′′ = Et).124 The only example of an authentic radical monoanion R′′-timdt™ has been isolated in compound S.72 Neutral 1,2-dithiolene ligands stabilized in the form of 3,4-disubstituted 1,2-dithietes have been characterized in few cases (R = CF3,120 COOCH3,121 1-(adamantyl)122). An examination of the ZPE-corrected total electronic energies εZPES of the neutral 1,2-dithiolene ligands in the dithione and dithieter forms (Table 2) shows that the dithieter form is more favored for the mnt ligand in comparison to the Me2timdt ligand (εZPES = 16.28 and −42.58 kcal/mol, respectively). A comparison of the C–C bond distances calculated for Me2timdt™ (dC−C = 1.500, 1.434, and 1.394 Å for q = 0, 1, and 2, respectively; Table 2) can be made with the corresponding bond distances determined structurally in [Pd(Et2timdt)Br2] (average dC−C value 1.47(1) Å; q = 0; Chart S2),5 (dC−C = 1.417(4) Å, q = 1; Chart S2),48 (6-2Br)2Br3Br2 (6 = 4,5,9,10-tetrahydro-[1,2-b:5,6-b′]-1,3,6,8-tetrahydridimidazo[2,7-d]thiophene; dC−C = 1.37(2) Å, q = 2; Chart S2), and 1,3-dimethyl-4,5-bis(phenylsulfonyl)-1,3-dihydro-2H-imidazole-2-thione (7, dC−C = 1.361(6) Å, q = 2; Chart S2).74 As expected, on passing from dianions to the corresponding neutral species the C–C bond lengths increase.
DFT IEF-PCM Level (CS GS) and Calculated Oscillator Strengths 

Under these conditions, the two possible spin states, i.e. \( S \) and \( \bar{S} \), consequently a negligible overlap integral is expected. The ground state (GS) of neutral bis(1,2-dithiolene) complexes is characterized by a significant spin contamination: \( S = 1 \) and \( \bar{S} = 3 \). When the energy difference \( \Delta_S = \varepsilon_S - \varepsilon_{\bar{S}} \) is not negligible and the two NBMOs are quasi-degenerate, the triplet configuration is the most stable (\( \varepsilon_S > \varepsilon_{\bar{S}} \)) and \( J \) assumes positive values in the so-called diradicaloids or diradical-like compounds. Wirz proposed discriminating between diradicals and diradicaloids depending on the singlet–triplet energy gaps (\( \Delta S \geq 10 \) and 100 kJ mol\(^{-1}\) for diradicals and diradicaloids, respectively).

The theoretical evaluation of the GS in diradical and diradicaloid species is a challenging task, which requires the evaluation of the stability of the triplet and singlet GSs of the investigated compound. The triplet GS can generally be calculated by theoretical methods with unrestricted wave functions, such as unrestricted HF (UHF) or density functional theory (UDFT). The modeling of open-shell singlet diradicals requires multireference approaches: for instance, multireference coupled-cluster calculations, such as Mukaiyama method, complete active space second-order perturbation theory (CASPT2).

### Table 1: Experimental NIR Absorption Maximum Wavelengths \( \lambda \) (nm), Energies \( E \) (eV), and FWHM Values \( \omega \) on a Wavelength Scale (nm) Recorded for 3, in Comparison with the Corresponding Values \( \lambda_{\text{calc}} \) and \( E_{\text{calc}} \) Calculated at the TD-DFT IEF-PCM Level (CS GS) and Calculated Oscillator Strengths \( f \), Extinction Coefficients \( \epsilon_{\text{calc}} \) (M\(^{-1}\) cm\(^{-1}\)), and HOMO–LUMO Energy Gaps \( \Delta E_{\text{H-L}} \) (eV) in Selected Solvents

| Solvent | \( \lambda \) | \( \lambda_{\text{calc}} \) | \( E \) | \( E_{\text{calc}} \) | \( \omega \) | \( f \) | \( \epsilon_{\text{calc}} \) | \( \Delta E_{\text{H-L}} \) |
|---------|-------------|----------------|--------|----------------|--------|---------|----------------|----------------|
| CHCl\(_3\) | 1006 | 876.0 | 1.167 | 1.416 | 180 | 0.385 | 10700 | 1.68 |
| CH\(_2\)Cl\(_2\) | 1020 | 863.8 | 1.216 | 1.436 | 151 | 0.368 | 11895 | 1.73 |
| THF | 1011 | 864.4 | 1.226 | 1.435 | 168 | 0.368 | 10675 | 1.71 |
| CH\(_2\)CN | 966 | 843.9 | 1.284 | 1.469 | 236 | 0.340 | 6630 | 1.77 |
| DMF | 955 | 851.8 | 1.298 | 1.456 | 217 | 0.356 | 7712 | 1.77 |

### Table 2: Optimized C–C and C–S Bond Distances (\( d_{\text{C-C}} \) and \( d_{\text{C-S}} \) A) within the 1,2-Dithiolen Moieties and Corresponding Wiberg Bond Indices (WBI\(_{\text{C-C}}\) and WBI\(_{\text{C-S}}\)), Variations in ZPE Corrected Total Electronic Energies \( \psi^0_{\text{ZPE}} = \varepsilon^0 + \text{ZPE} \), kcal mol\(^{-1}\), Sum of Electronic Energies and Thermal Enthalpies \( (H_{\text{corr}} \text{ kcal mol}^{-1}) \), and Free Energies \( (G_{\text{corr}} \text{ kcal mol}^{-1}) \) Calculated for the 1,2-Dithiole Ligands mnt\(^{\text{ff}}\) and Me\(_2\)timdt\(^{\text{ff}}\) (q = 0, 1, 2)

| \( q \) | \( d_{\text{C-C}} \) | \( d_{\text{C-S}} \) | WBI\(_{\text{C-C}}\) | WBI\(_{\text{C-S}}\) | \( \Delta \psi^0_{\text{ZPE}} \) | \( \Delta \varepsilon^0 \) | \( \Delta \psi^0_{H_{\text{corr}}} \) | \( \Delta \psi^0_{G_{\text{corr}}} \) |
|-------|----------|----------|-------------|-------------|----------------|-----------|----------------|----------------|
| 0 | 1.501 | 1.625 | 1.018 | 1.787 | | | | |
| 1 | 1.371 | 1.766 | 1.501 | 1.100 | −16.28 | −16.85 | −15.46 | |
| 2 | 1.343 | 1.765 | 1.538 | 1.061 | 42.58 | 41.28 | 45.27 | |
| 0 | 1.431 | 1.681 | 1.397 | 1.235 | −84.47 | −84.58 | −84.09 | |
| 1 | 1.431 | 1.675 | 1.217 | 1.423 | −51.33 | −51.35 | −50.90 | |
| 2 | 1.406 | 1.736 | 1.365 | 1.178 | −34.75 | −34.87 | −33.87 | |
| 0 | 1.394 | 1.738 | 1.453 | 1.201 | 13.07 | 13.09 | 14.23 | |

and the C–S distances decrease. It is worth noting that mnt\(^{\text{ff}}\) and Me\(_2\)timdt\(^{\text{ff}}\) (q = 0, 1, 2) share closely related frontier MOs. The singlet (2S + 1 = 1) and triplet (2S + 1 = 3), are degenerate, their energy difference \( \Delta S_T = \varepsilon_S - \varepsilon_{\bar{S}} \) being related to the exchange interaction \( J = 1/2(\varepsilon_S - \varepsilon_{\bar{S}}) = 1/2 \Delta E_{S_T} \). When \( S_{\text{ab}} \) is not negligible and the two NBMOs are quasi-degenerate, the triplet configuration is the most stable (\( \varepsilon_S > \varepsilon_{\bar{S}} \)) and \( J \) assumes positive values in the so-called diradicaloids or diradical-like compounds. Wirz proposed discriminating between diradicals and diradicaloids depending on the singlet–triplet energy gaps (\( \Delta_S > 10 \) and 100 kJ mol\(^{-1}\) for diradicals and diradicaloids, respectively). When the energy difference between the two involved MOs is larger and a significant gap exists, the energy stabilization competes with the electron–electron exchange interaction, and the GS singlet GS becomes progressively more stable. The theoretical evaluation of the GS in diradical and diradicaloid species is a challenging task, which requires the evaluation of the stability of the triplet and singlet GSs of the investigated compound. The triplet GS can generally be calculated by theoretical methods with unrestricted wave functions, such as unrestricted HF (UHF) or density functional theory (UDFT). The modeling of open-shell singlet diradicals requires multireference approaches: for instance, multireference coupled-cluster calculations, such as Mukaiyama method, complete active space second-order perturbation theory (CASPT2).

### Diradical Character (DC) in Bis(1,2-dithiole) Complexes

The ground state (GS) of neutral bis(1,2-dithiole) complexes is characterized by a significant degree of DC, due to the very narrow HOMO–LUMO energy gap \( \Delta E_{H-L} \) that renders the singlet and triplet GSs very close in energy. In a pure diradical the nonbonding molecular orbitals (NBMOs) \( \psi_1 \) and \( \psi_2 \), hosting the two electrons at the highest energy are degenerate, being localized on the two different ligands in bis(1,2-dithiole) metal complexes, and they have consequently a negligible overlap integral \( S_{\text{ab}} = \langle \psi_1 \psi_2 \rangle \). Under these conditions, the two possible spin states, i.e. singlet (2S + 1 = 1) and triplet (2S + 1 = 3), are degenerate, their energy difference \( \Delta S_T = \varepsilon_S - \varepsilon_{\bar{S}} \) being related to the exchange interaction \( J = 1/2(\varepsilon_S - \varepsilon_{\bar{S}}) = 1/2 \Delta E_{S_T} \). When \( S_{\text{ab}} \) is not negligible and the two NBMOs are quasi-degenerate, the triplet configuration is the most stable (\( \varepsilon_S > \varepsilon_{\bar{S}} \)) and \( J \) assumes positive values in the so-called diradicaloids or diradical-like compounds. Wirz proposed discriminating between diradicals and diradicaloids depending on the singlet–triplet energy gaps (\( \Delta_S > 10 \) and 100 kJ mol\(^{-1}\) for diradicals and diradicaloids, respectively). When the energy difference between the two involved MOs is larger and a significant gap exists, the energy stabilization competes with the electron–electron exchange interaction, and the GS singlet GS becomes progressively more stable. The theoretical evaluation of the GS in diradical and diradicaloid species is a challenging task, which requires the evaluation of the stability of the triplet and singlet GSs of the investigated compound. The triplet GS can generally be calculated by theoretical methods with unrestricted wave functions, such as unrestricted HF (UHF) or density functional theory (UDFT). The modeling of open-shell singlet diradicals requires multireference approaches: for instance, multireference coupled-cluster calculations, such as Mukaiyama method, complete active space self-consistent field (CASSCF), or the complete-active-space second-order perturbation theory (CASPT2).

### Inorganic Chemistry

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17390
Table 3. Optimized Pd–S, C−C, and C−S Bond Lengths (d, Å) and Wiberg Bond Indices (WBI) within the 1,2-Dithiolene Ligands L and \( L' \) of \([\text{Pd}(L)(L')_2]\) Complexes (\( L = L' = \text{Me}_2\text{timdt} \) for \( 1^q \); \( L = \text{Me}_2\text{timdt}, L' = \text{mnt} \) for \( 3^q \); \( L = L' = \text{mnt} \) for \( 4^q \); \( q = 0, 1, 2 \))

| GS            | symm  | \( d_{\text{Pd-S}} \) | \( d_{\text{C-C}} \) | \( d_{\text{C-S}} \) | WBI\(_{\text{C-C}} \) | WBI\(_{\text{C-S}} \) | \( d_{\text{Pd-S}} \) | \( d_{\text{C-C}} \) | \( d_{\text{C-S}} \) | \( \Delta d_{\text{C-C}} \) | WBI\(_{\text{C-C}} \) | WBI\(_{\text{C-S}} \) |
|---------------|-------|-------------------------|-----------------------|-----------------------|-----------------|-----------------|-------------------------|-------------------------|-------------------------|-----------------|-----------------|-----------------|
| \([\text{Pd}(\text{Et}_2\text{timdt})_2]\) (structural data) \( ^{a, e} \) |       |                         |                       |                       |                 |                 |                         |                       |                       |                 |                 |                 |
| \( 1^− \)     | triplet \( ^3\text{B}_1u \) | 2.351                   | 1.410                 | 1.698                 | 1.177           | 1.378           |                         |                       |                       |                 |                 |                 |
|               | singlet \( ^1\text{A}_1 \)   | 2.314                   | 1.404                 | 1.697                 | 1.269           | 1.276           |                         |                       |                       |                 |                 |                 |
|               | BS                  | 2.307                   | 1.401                 | 1.699                 | 1.251           | 1.274           |                         |                       |                       |                 |                 |                 |
| \( 1^2− \)    | doublet \( ^3\text{B}_2g \)  | 2.337                   | 1.381                 | 1.717                 | 1.385           | 1.192           |                         |                       |                       |                 |                 |                 |
|               | singlet \( ^1\text{A}_g \)   | 2.376                   | 1.365                 | 1.739                 | 1.482           | 1.126           |                         |                       |                       |                 |                 |                 |
| \( 3 \)       | triplet \( ^3\text{B}_1 \)   | 2.359                   | 1.408                 | 1.700                 | 1.226           | 1.267           | 2.305                   | 1.404                   | 1.701                   | 0.004           | 1.307           | 1.098           |
|               | singlet \( ^1\text{B}_1 \)   | 2.342                   | 1.428                 | 1.674                 | 1.168           | 1.397           | 2.263                   | 1.393                   | 1.725                   | 0.035           | 1.417           | 1.098           |
|               | BS                  | 2.344                   | 1.422                 | 1.682                 | 1.186           | 1.354           | 2.273                   | 1.389                   | 1.717                   | 0.033           | 1.384           | 1.098           |
| \( 3 \) (structural data) \( ^{a, e} \) |       |                         |                       |                       |                 |                 |                         |                       |                       |                 |                 |                 |
| \( 3^− \)     | doublet \( ^3\text{A}_1 \)   | 2.369                   | 1.397                 | 1.697                 | 1.290           | 1.276           | 2.286                   | 1.376                   | 1.740                   | 0.021           | 1.451           | 1.138           |
|               | singlet \( ^1\text{B}_1 \)   | 2.384                   | 1.364                 | 1.737                 | 1.477           | 1.131           | 2.323                   | 1.381                   | 1.744                   | −0.017          | 1.424           | 1.130           |
| \( 4 \)       | triplet \( ^3\text{B}_1u \)  | 2.325                   | 1.410                 | 1.696                 | 1.277           | 1.329           |                         |                       |                       |                 |                 |                 |
|               | singlet \( ^1\text{A}_g \)   | 2.275                   | 1.403                 | 1.701                 | 1.325           | 1.305           |                         |                       |                       |                 |                 |                 |
|               | BS                  | 2.289                   | 1.451                 | 1.699                 | 1.311           | 1.312           |                         |                       |                       |                 |                 |                 |
| \( 4^− \)     | doublet \( ^3\text{B}_2g \)  | 2.295                   | 1.386                 | 1.725                 | 1.405           | 1.195           |                         |                       |                       |                 |                 |                 |
|               | singlet \( ^1\text{A}_g \)   | 2.332                   | 1.380                 | 1.743                 | 1.428           | 1.131           |                         |                       |                       |                 |                 |                 |
| \( 4 \) (structural data) \( ^{a, e} \) |       |                         |                       |                       |                 |                 |                         |                       |                       |                 |                 |                 |

\( ^a \) For neutral species \( (q = 0) \), the distances in the open-shell paramagnetic triplet, CS diamagnetic singlet, and singlet diradical (BS) configurations are reported. \( ^b \) GS-symmetry representations are referenced to the \( D_{\text{sh}} \) (1, 4) and \( C_{\text{v}} \) (3) point groups, with the complex molecule laying on the \( yz \) plane and the main axis being coincident with \( z \). \( ^c \) Reference 45. \( ^d \) Average value. \( ^e \) This work. \( ^f \) Isolated in (perylene \(_2\)). Reference 116.
the total spin $\langle S \rangle$ with respect to $\langle S(S + 1) \rangle$. In different studies, the DC index $n_{DC}$ of homoleptic bis(1,2-dithiolene) complexes was evaluated. A comparison of $n_{DC}$ calculated at different levels of theory suggests that the DFT-BS approach underestimates the DC of bis(1,2-dithiole) metal complexes. In fact, the DC of the neutral complex [Ni(bdt)₂] (bdt⁻² = benzene-1,2-dithiole) was calculated to be as large as 69.1% at the CASSCF level, and 32% at the ZORA-SORCI level (ZORA = zeroth-order regular approximation; SORCI = spectroscopy oriented configuration interaction), and 17.2% at the DFT-BS level. The DC depends not only on the 1,2-dithiolene ligand but also on the nature of the central metal ion. In the series of complexes of M⁺ ions derived from the 3,5-di-tert-butyl-1,2-benzene-dithiolato ligand, the $n_{DC}$ values were calculated to be 32%, 50%, and 30% for $M = \text{Ni}, \text{Pd}, \text{Pt}$, respectively, suggesting that Pd₃ species may show particularly stable singlet radicals in comparison to the corresponding Ni²⁺/Pt²⁺ analogues.

**Homoleptic Bis(1,2-dithiolene) Complexes.** Members of the class of complexes $[M(K_2timdt)_2]$ $^\omega$ ($M = \text{Ni}, \text{Pd}, \text{Pt}; q = 0, 1, 2)$ are mostly stable as neutral species, and quite severe conditions are needed to achieve a reversible chemical or electrochemical reduction to the corresponding monoaionic radical species. With regard to $M = \text{Pd}$, while the crystal structures of [Pd(Et₂timdt)₂] and the CT adduct [Pd(Et₂timdt)₂]I CH₃Cl have long since been published, no anionic complexes [Pd(R₂timdt)₂]⁻²⁻ have been structurally characterized so far. Conversely, neutral [M(mnt)₂] complexes ($M = \text{Ni}, \text{Pd}, \text{Pt}$) are extremely rare, and (perylenyl)$_2$(4) is the only compound characterized structurally incorporating the neutral species, while to date 37 examples of compounds incorporating the anions $4^{-2}$⁻ have been deposited with the Cambridge Crystallographic Database. Accordingly, 1 is calculated to be sensibly more stable to reduction in the gas phase and in CH₂Cl₂ than 4 ($E_{S \rightarrow BS}^{100K} = 3.057$ and 4.349 eV for complex 1 and 4.786 and 5.752 eV for complex 4, in the gas phase and in CH₂Cl₂, respectively). In Table 3, the metric parameters optimized for the bis(1,2-dithiolene) complexes 1⁻⁻ and 4⁻⁻ ($q = 0, 1, 2$) are summarized. In the case of neutral complexes ($q = 0$), the geometry was optimized (i) for the singlet CS (RDFT), (ii) for the triplet open-shell (UDFT), and (iii) for the singlet diradical (DFT-BS) GS configurations. The total electronic energy $\varepsilon_1$ of the $^{3}B_{1u}$ triplet state is calculated to be lower by about 2.4 kcal mol⁻¹ (10 kJ mol⁻¹) in comparison to that ($\varepsilon_0$) of the uncorrected singlet $^{1}A_{g}$ GS ($\varepsilon_2 < 0$, eq 2), thus classifying 1 as a diradical species. In fact, the DFT-BS GS of 1 shows a large $\langle S \rangle_{BS}$ value (0.80, Table 4), indicating a considerable spin contamination from the triplet state. An evaluation of the total electronic energy of the BS GS shows that it is the most stable configuration in comparison to both the triplet and CS-singlet configurations (eq 1), reflected by the diradical character $n_{DC} = 55.4\%$ (Table 4, eq 5). The singlet GS calculated for 4 is sensibly lower in energy in comparison to the relevant triplet state (Table 4), indicating a diradicaloid character. Accordingly, the singlet diradical configuration is only slightly more stable than the uncorrected CS singlet state and has an $\langle S \rangle_{BS}$ value smaller than 0.5. In fact, the spin-contamination corrected state (eq 4) was found to be the most stable state with only a partial diradical character ($n_{DC} = 27.5\%$, Table 4). A comparison between structural and DFT-optimized bond distances for complexes 1 and 4 shows that the Pd⁻⁻S and C⁻⁻C distances are slightly overestimated, while C⁻⁻S bond lengths are very close. Pd⁻⁻S bond lengths are very sensitive to the GS configuration and follow the trend Pd⁻⁻S (triplet) > Pd⁻⁻S (CS singlet) ≥ Pd⁻⁻S (diradical) > Pd⁻⁻S (structure). The C⁻⁻S bond distances optimized for the singlet diradical GSs of 1 and 4 (1.699 Å; Table 3) are very close to those calculated for the hypothetical free Me₂timdt⁻²⁻ and mnt⁻²⁻ radical anions (1.681 and 1.675 Å, respectively) but remarkably different from those calculated for the relevant 1,2-dithiones and 1,2-dithiolates (Table 2). This supports the description of neutral homoleptic complexes as [Pd(L⁺⁻⁻)], for both classes of complexes. Although the agreement between structural and optimized C⁻⁻C distances is less accurate in comparison to C⁻⁻S bond lengths, the former values are affected very greatly by the charge on the ligands. In Figure 3, the optimized C⁻⁻C distances and the corresponding Wiberg bond indices (WBI) are compared for a variety of K₂timdt derivatives showing a C⁻⁻C double bond, as in 4,5,9,10-tetraethiocin[1,2-b:5,6-b’]diimidazolyl-1,3,6,8-tetramethyl-2,7-dithione (Me₂timdt)₂ and compound 7, or a single bond, as in the neutral complex 2 and in compound 5 (Chart S2). For these compounds, a clear correlation ($R^2 = 0.99$) holds between the optimized C⁻⁻C bond distance $d_{C-C}$ and the corresponding WBI for C⁻⁻C. This clearly shows that WBIs calculated at the optimized distances

**Table 4. Energy Differences (kcal mol⁻¹) between the Singlet and the Broken-Symmetry Configurations ($\varepsilon_1$), the Singlet and the Triplets Configurations ($\varepsilon_2$), the Spin Contamination Corrected Singlet and the Triplet Configurations ($\Delta E_{ST}$), Expectation Value of the Spin Contaminant ($\langle S \rangle_{BS}$), and the Singlet Diradical Configuration, Effective Electron Exchange Integrals $J_{ab}$ and Diradical Characters $n_{DC}$ (%) Calculated for Complexes 1, 3, and 4**

|   | 1 | 3 | 4 |
|---|---|---|---|
| $\varepsilon_1$ | -4.325 | -0.789 | -1.015 |
| $\varepsilon_2$ | -2.404 | 5.817 | 6.197 |
| $\Delta E_{ST}$ | 3.986 | -7.420 | -8.096 |
| $\langle S \rangle_{BS}$ | 0.801 | 0.436 | 0.474 |
| $J_{ab}$ | 1.579 | 4.175 | 4.664 |
| $n_{DC}$ | 55.4 | 24.9 | 27.5 |

**Figure 3. Correlation between optimized C⁻⁻C bond distances ($d_{C-C}$) and Wiberg bond indices (WBI) within the 1,2-dithiole ligand for selected systems (circle, singlet; star, doublet; triangle, triplet; square, singlet diradical).**
represent a reliable parameter for evaluating the charge distribution and hence the oxidation state of noninnocent 1,2-dithiolene ligands. When 1,2-dithiolene complexes 1$^+$ (q = 0, 1, 2) are considered, the d$_{C-C}$ and WBI$_{C-C}$ data, while not exactly fitting the correlation, point out that complex 1$^+$ falls in the area of C=C double bonds, very close to (Me$_2$timdt)$_2$ and compound 7, therefore confirming the 2-thioximidazoline-4,5-dithiolate nature of the ligands in the dianionic complex. Complexes 1 (whatever the approach adopted for describing its GS) and 1$^+$ fall in the central area of the graph, indicating an intermediate character of the C−C bond between a single and a double bond.

An examination of the frontier KS-MOs composition shows that, according to the CS description of the GS of 1, the KS-HOMO and the KS-LUMO are $\pi$-MOs represented by the b$_{3u}$ in-phase and b$_{2g}$ out-of-phase combinations of the singly occupied molecular orbitals (SOMOs) of the two Me$_2$timdt$^{**}$ ligands (Figure 4a and Figure S8). In fact, the b$_{3u}$ KS-HOMO (MO 107 according to a progressive labeling based on an energy scale) is mainly made up of the four 3$p_x$ AOs of the four donor S atoms, perpendicular to the molecular $yz$ plane, and the four C 2$p_z$ AOs taken with opposite phases. The terminal S atoms also participate in this MO, while the contribution from the central Pd ion is very poor (4%). The 108 b$_{2g}$ KS-LUMO involves the same atomic species as the HOMO with a larger contribution from the bonding sulfur atoms, but the contributions from the two ligands are opposite in phase. In the KS-LUMO, the metal ion is only marginally involved (5%) as well through its 3$d_{yz}$ AOs. In the singlet diradical DFT-BS GS configuration, the $\alpha$- and $\beta$-HOMOs show the same composition as the HOMOs of the constituent 1,2-dithiolene Me$_2$timdt$^{**}$ ligands, analogously to what was previously reported for different Ni and Pt bis(1,2-dithiolene) metal complexes. The central Pd ion participating to both $\alpha$ and $\beta$ MOs (3%). Notably, the DFT-BS approach results in a stabilization of the KS-HOMO and destabilization of the KS-LUMO with respect to the restricted CS solution, thus increasing the $\Delta E_{\text{BS-L}}$ gap (Figure 5, top). The CS description of complex 1 features a single allowed NIR one-electron excitation calculated at the TD-DFT level. This corresponds to the $^1A_g \rightarrow ^1B_{1u}$ transition, involving almost exclusively (97%) the one-electron HOMO−LUMO (H → L) excitation. This is calculated to fall at 963.0 nm (oscillator strength $f = 0.436$) in the gas phase and 1068.3 nm ($f = 0.581$) in CH$_2$Cl$_2$. The oscillator strength calculated at the TD-DFT level along with the experimental FWHM value of the NIR band were used to evaluate the molar extinction coefficient $\varepsilon$ for 1 (eq 6). The symmetric and antisymmetric combinations of the $\alpha$ and 108 and $\beta$ excitations (H$H$ → L$L$ double exciton states) are calculated as BS-GS → ES 1 and BS-GS → ES 2 transitions. Double exciton states have been reported for conjugated chromophores with open-shell diradical character, such as polyenes and quinoidal oligothiophenes. The double exciton state is one-photon forbidden, and it has been observed as a weak band at lower energies in comparison to the main absorption band due to the one-photon allowed single exciton state. The symmetry-allowed transition BS-GS → ES 2 falls at wavelength values lower ($E = 1.487$ eV, $\lambda_{\text{max}} = 833.6$ nm, $f = 0.310$) than those predicted for the singlet GS (see above). The complex envelope of the NIR absorption band of neutral [M(R,R’timdt)$_2$] bis(1,2-dithiolene) complexes can be attributed to the contribution of doubly excited states to the main single exciton states, thus possibly accounting for the unusually high molar extinction coefficients observed for the NIR absorption in this class of bis(1,2-dithiolene) complexes. The forbidden BS-GS → ES 1 transition ($1.142$ eV, $\lambda_{\text{max}} = 1085.6$ nm) may provide a low-energy weak contribution to the NIR absorption due to the vibronic coupling with the b$_{3u}$ antisymmetric combination of the stretching Pd–S vibrations, calculated at 294.1 and 293.2 cm$^{-1}$ at the RDFT and DFT-BS levels, respectively.

Figure 4. Qualitative MO diagram showing the contributions of the HOMOs of the 1,2-dithiolene ligands to the HOMO and LUMO of complex 1 (a; $c_1 = 48%$, $c_2 = 4%$, $c_3 = 47.5%$, $c_4 = 5%$) and complex 3 (b; $c_1 = 61%$, $c_2 = 31%$, $c_3 = 8%$, $c_4 = 24%$, $c_5 = 70%$, $c_6 = 6%$) in the CS GS description. In the KS-MO drawings hydrogens have been omitted for clarity. Cutoff value: 0.05 lel.

Figure 5. Frontier KS-MO energy diagram (−2 to −8 eV) showing the energy and MO drawing in the restricted (CS GS, left) and singlet diradical (BS GS, right) descriptions for 1 (top) and 3 (bottom). Cutoff value: 0.05 lel.
Electronic Structure of [Pd(Me₂timdt)(mnt)] (3). The GS geometry for 3 ($E_{\text{Abs}}^\text{MO} = 3.784$ and $4.872$ eV in the gas phase and CH₂Cl₂, respectively) was optimized in its singlet CS ($^1\text{B}_1$), triplet open shell ($^3\text{B}_1'$), and singlet diradical (BS) configurations. The triplet–singlet energy gap classifies 3 as a diradicaloid (Table 4).

While the $^3\text{B}_1'$ state is sensibly less stable than the singlet state, the singlet diradical BS ($S^2$) is 0.436 eV and the $^1\text{B}_1$ CS singlet configurations differ by less than 1 kcal mol$^{-1}$ (Table 4). The singlet configurations calculated at the DFT and DFT-BS levels show very close optimized Pd–S, C–C, and C–S bond distances, only very slightly overestimated (by less than 0.03 Å) in comparison to the relevant structural distances (Table 3). The difference $\Delta d_{\text{C-C}}$ between the C–C bond distances $d_{\text{C-C}}$ of the two 1,2-dithiolene ligands (corresponding to the C(1)–C(1)' and C(4)–C(4)' structural bond lengths in Figure 1 for the Me₂timdt and mnt ligands, respectively) is evaluated correctly being better described as a dithione-dithiolato [PdII(Me₂timdt)–]

Therefore, both the DFT and DFT-BS approaches agree in attributing an LLCT character to the lowest energy transition, from the mnt “pull” ligand to the Me₂timdt “push” ligand. TD-DFT calculations show, in excellent agreement with experimental data (Figure 2 and Figure S3 in the Supporting Information), three main spectral regions, namely (i) an overlap of intense transitions in the UV region ($\lambda < 280$ nm), (ii) a band in the visible region (300 $\leq \lambda \leq 500$ nm), and (iii) a single very intense NIR transition ($\lambda > 800$ nm). In Figure 6,
of theory in the same solvent systems experimentally adopted to record UV–vis−NIR spectra. The calculated NIR transition energies are generally overestimated but are linearly correlated to the experimental energies \( (R^2 = 0.88; E_{\text{calc}} (\text{eV}) = 0.374; E_{\text{exp}} + 0.979; \text{Table 1 and Figure S10}) \). Both in the gas phase and in the solvents considered at the IEF-PCM TD-DFT level, the NIR transition is attributed exclusively to the H \( \rightarrow \) L one-electron excitation. Accordingly, a linear correlation holds between the calculated transition energies in the NIR region and the \( \Delta E_{\text{H+1-L}} \) energy gap evaluated in each of the examined solvents (Table 1; \( R^2 = 0.92 \)). Along the series CHCl\(_3\), CH\(_2\)Cl\(_2\), THF, CH\(_3\)CN, and DMF the contribution of the mnt fragment to KS-HOMO and KS-LUMO slightly increases (68% to 70%) and decreases (16% to 13%), respectively (Table S7). The contribution of the Me\(_2\)timdt fragment to the KS-HOMO and to the KS-LUMO decreases (23% to 20%) and increases (78% to 82%), respectively. Therefore, on passing to CHCl\(_3\) to DMF, the NIR transition assumes a larger LL'C'T character, and the \( \Delta E_{\text{H+1-L}} \) energy gap increases from 1.68 eV in CHCl\(_3\) to 1.77 eV in DMF and CH\(_3\)CN, in agreement with the experimental trend of NIR absorption energies (Table 1). Calculated oscillator strengths \( f \) fall between 0.356 and 0.385 in DMF and CHCl\(_3\), reaching the same order of magnitude computed for \( \text{HOMO} (H) = 0.10 \). Excited state (ES) numbering taken from gas-phase calculations.

### Table 5. Energies \( E \) (eV), Wavelengths \( \lambda \) (nm), and Oscillator Strengths \( f \) of the Main (\( f \geq 0.005 \)) UV–vis−NIR Electronic Transitions Calculated for 3 in the Gas Phase and in CH\(_2\)Cl\(_2\) and CHCl\(_3\) at the IEF-PCM TD-RDFT Level\(^a\)

| ES\(^b\) symm | gas phase | CHCl\(_3\) | CH\(_2\)Cl\(_2\) | main contribution |
|-------------|-----------|----------|-----------------|------------------|
| \( 3\)     | \( 1\)     | 1.489    | 832.6           | 0.315            | \( 1.415 \)          |
| \( \alpha\) | \( 1\)     | 2.931    | 423.0           | 0.153            | \( 2.950 \)          |
| \( \beta\)  | \( 1\)     | 2.983    | 315.7           | 0.009            | \( 2.962 \)          |
| \( \alpha\) | \( 1\)     | 3.586    | 345.8           | 0.096            | \( 3.691 \)          |
| \( \beta\)  | \( 1\)     | 3.787    | 327.4           | 0.046            | \( 3.616 \)          |
| \( \alpha\) | \( 1\)     | 4.133    | 300.1           | 0.121            | \( 4.315 \)          |
| \( \beta\)  | \( 1\)     | 4.364    | 284.2           | 0.005            | \( 4.294 \)          |
| \( \alpha\) | \( 1\)     | 1.973    | 812.6           | 0.315            | \( 1.950 \)          |
| \( \beta\)  | \( 1\)     | 2.993    | 423.0           | 0.153            | \( 2.950 \)          |
| \( \alpha\) | \( 1\)     | 3.586    | 345.8           | 0.096            | \( 3.691 \)          |
| \( \beta\)  | \( 1\)     | 3.787    | 327.4           | 0.046            | \( 3.616 \)          |
| \( \alpha\) | \( 1\)     | 4.133    | 300.1           | 0.121            | \( 4.315 \)          |
| \( \beta\)  | \( 1\)     | 4.364    | 284.2           | 0.005            | \( 4.294 \)          |

\( ^a \)ES-HOMO (H) = MO 93; KS-LUMO (L) = MO 94. \( \beta \)Excited state (ES) numbering taken from gas-phase calculations.

**CONCLUSIONS**

DFT calculations have been exploited to investigate the structural and spectroscopic features of the heteroleptic mixed-ligand neutral complex Pd\(^{11}\) bis(1,2-dithiole) 3, to highlight the differences between the homoleptic related complexes 1 and 4 and to develop sound structure–property relationships. The closed-shell (CS) description is only partially suitable to describe the electronic structure of bis(1,2-dithiole) complexes, and—whatever the nature of the ligands—the singlet diradical character (DC) must be taken into account. The broken-symmetry (BS) approach within DFT, although itself a dramatic approximation underestimating the DC of bis(1,2-dithiole) metal complexes, is a useful tool in supplementing the description of the ground state (GS). A few general conclusions can be drawn

1. The nature of the 1,2-dithiole ligand is responsible for the relevance of diradical character (DC) in the GS of 1,2-dithiole complexes. In homoleptic neutral bis(1,2-dithiole) complexes, on passing from complex 4 to complex 1, the n(DC) index is roughly doubled. This can
be related to the capability of the ligands mnt\(^{−}\) and Me\(_2\)timdt\(^{−}\), respectively, to stabilize the unpaired electron. In heteroleptic mixed-ligand complexes, the absolute one-electron-reduction potentials \(E_{\text{Abs}}^{298K}\) calculated for the \(L/L^{−}\) and \(L'/L'^{−}\) couples can be used to evaluate the nature of the \([\text{Pd}^{\text{II}}(L)(L')]\) complex. The 1,2-dithiolene ligand displaying the largest reduction potential (‘pull’ ligand) features its \(\pi\)-NBMO at lower energy and contributes largely to the KS-HOMO of the heteroleptic complex, while that with the lowest potential (‘pull’ ligand) contributes to the KS-LUMO. As a consequence, it is conceivable that the difference \(\Delta E_{\text{Abs}}^{298K}\) in the absolute reduction potentials of the ligands \(L\) and \(L’\) can be adopted as a useful parameter to estimate the push–pull nature of the resulting heteroleptic neutral complexes \([\text{Pd}^{\text{II}}(L)(L')]\) and the different localizations of the KS-HOMO and KS-LUMO. A larger push–pull character points to a larger dithione-dithiolato nature and a lower DC of the complex. This implies that the DC is the largest in homoleptic bis(1,2-dithiolene) complexes \([\text{Pd}^{\text{II}}(L)_2]\) with ligands \(L\) featuring low values of \(E_{\text{Abs}}^{298K}\), such as Me\(_2\)timdt, and decreases in heteroleptic complexes \([\text{Pd}^{\text{II}}(L)(L')]\) in dependence on \(\Delta E_{\text{Abs}}^{298K}\).

(2) Several authors have observed that metal–sulfur bond lengths optimized at the DFT level are slightly overestimated in comparison to structural bond distances. This can be attributed to the use of RDFT calculations in complexes featuring a significant DC. The DFT-BS approach leads to bond distances closer to the structural distances. It can be deduced that, in the case of complexes with a large DC, such as complex 1, the difference between CS-optimized distances and the relevant experimental metric parameters increases with the DC of the complex.

(3) The spectral shape of the NIRD band of neutral bis(1,2-dithiolene) metal complexes has been indicated to be a complex envelope resulting from a series of d–d transitions with different spin couplings to the open-shell ligands. The intensity of this band, peculiar to metal bis(1,2-dithiolene) complexes, may be attributed not only to the very large oscillator strength \(f\) calculated for the HOMO–LUMO one-electron excitation within a CS description but also to the contribution of double exciton states typical of diradical species. To a lower extent, double exciton states are possible also in heteroleptic bis(1,2-dithiolene) complexes and can be related to the spectral shapes observed for the NIRD band in different solvents.

(4) The intrinsic optical nonlinearity of heteroleptic bis(1,2-dithiolene) complexes is enhanced by their DC, providing a further criterion, in addition to the lack of an inversion center and large electric dipole moment values, for the rational design of NLO materials active in the vis–NIR region.

Summarily, this investigation shows that the DC of bis(1,2-dithiolene) metal complexes can be extensively modulated by means of the choice of the substituents R at the 1,2-dithiolene core, allowing for the rational design of the linear and nonlinear optical properties of the resulting complexes and hence the possibility of applying them in fields as varied as nonlinear optics, photoconductivity, and electrochromism.

Further studies are ongoing in our laboratory to investigate in detail the role of the central metal ion and to generalize the limited findings described here for the Pd\(^{\text{II}}\) complexes with the mnt and Me\(_2\)timdt ligands to other homoleptic and heteroleptic bis(1,2-dithiolene) complexes differing in the nature of the central metal ions and 1,2-dithiolene ligands.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02696.

Details on theoretical calculations, molecular schemes for the compound discussed in the paper, crystallographic data and packing details for complex 3, experimental UV–vis–NIR spectra decomposed into their component Gaussian peaks, NIR spectra and IR spectra in MeCN, DMSO, THF, CH\(_2\)Cl\(_2\), and CHCl\(_3\), KS frontier MO drawings calculated for Me\(_2\)timdt\(^{−}\), mnt\(^{−}\) \((q = 0, 1, 2)\), and complex 3, RDFT, DFT-BS, and (IEF-PCM) TD-DFT data for 1 and 3, and calculated second-order hyperpolarizabilities \(\beta\) and dipole moments \(\mu\) (PDF)

#### Accession Codes

CCDC 2027023 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
The authors declare no competing financial interest.

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ABBREVIATIONS
BS, broken symmetry; CS, closed shell; DC, diradical character; GS, ground state; MO, molecular orbital; HOMO, highest occupied molecular orbital; KS, Kohn–Sham; LUMO, lowest unoccupied molecular orbital; NBMO, nonbonding molecular orbital; NLO, nonlinear optics; SONLO, second-order nonlinear optics.

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