A Facile Synthesis of a Push-Pull Mixed-Ligand Pd-Dithiolene Complex Containing the Et_2timdt Ligand (Et_2timdt = Monoreduced Diethylimidazolidine-2,4,5-trithione)

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The reaction of the dithiolene [Pd(Et_2timdt)$_2$] (Et_2timdt = formally monoreduced diethylimidazolidine-2,4,5-trithione) with Br_2 or IBr yields the complex [Pd(Et_2timdt)Br_2], a good starting material for the synthesis of novel push-pull mixed-ligand Pd-dithiolenes. The synthesis and characterisation of the unsymmetrical dithiolene [Pd(Et_2timdt)(mnt)] (mnt = maleonitriledithiolato dianion) is also reported.

In recent years, non-linear optical (NLO) materials have attracted great interest because of their wide range of possible applications in several fields, such as laser technology, telecommunications, data storage, and optical switches.[1] So far, most reports have dealt with inorganic and organometallic compounds with extended delocalized π-systems.[2] Among these, "non-innocent"[3] metal-dithiolenes represent a very promising class of compounds in view of their peculiar electronic structure accompanied by high thermal and photochemical stabilities.[4]

Recently, we have reported a new class of neutral dithiolenes [M(R,R′timdt)$_2$] (M = Ni, Pd, Pt),[5] which shows remarkable stability and an unusually intense NIR absorption at about 1000 nm, whose energy is tunable by changing the metal ion and/or substituents R and R′.[6–9] The intense NIR absorption makes these dithiolenes good candidates as Q-switching and/or mode-locking dyes in the technology of Nd-lasers (such as Nd:YLF and Nd:YAG, emitting at 1053 and 1064 nm, respectively), and for applications in solid-state NIR-photodetectors.[10] These compounds are structurally analogous to the metal dithiolenes that derive from the ligand dmit (dmit = 2-thioxo-1,3-dithiol-4,5-dithiolate), while differing in that NR groups are present instead of endocyclic S atoms in the heterocyclic organic framework of the ligand.[11] However, while [M(R,R′timdt)$_2$] dithiolenes are isolated in the neutral state, [M(dmit)$_2$] complexes have been reported as anions with integer or fractional charges, and have been used as building blocks to prepare materials with interesting conducting properties.[12,13]

DFT calculations have confirmed that the terminal sulfur atoms in the two classes of dithiolenes are differently charged: those in the neutral [M(dmit)$_2$] dithiolenes carry a small positive charge, while those in the neutral [M(R,R′timdt)$_2$] dithiolenes carry a non-negligible negative charge.[8] The donor properties of the latter complexes have been exploited in the reactions with iodine: the interaction of I_2 at the terminal sulfur atoms gives CT adducts bearing linear S−I−I groups.[6,7] The reactions of [Ni(R,R′timdt)$_2$] with Br_2 and IBr generally occur with elimination of the central Ni ion. For example, in the case of the reaction of [Ni(*i*Pr_2timdt)$_2$] with IBr, together with other unidentified by-products, the corresponding 1,3,6,8-tetrasubstituted 4,5,9,10-tetrathiocino-[1,2-*b*:5,6:*b*′]diimidazolyl-2,7-dithione was identified by X-ray diffraction.[14]

Unexpectedly, the reaction between [Pd(Et_2timdt)$_2$] (**1**)[7] and either IBr or Br_2 in molar ratios ranging from 1:1 to 1:20 gave very tiny bronze crystals, with an elemental analysis that corresponds to the formula of [Pd(Et_2timdt)Br_2] (**2**). Although the quality of these crystals was not good enough to obtain reliable structural data (see Exp. Sect.), it is possible to note that on passing from **1** to **2**, the Pd ion maintains a square-planar coordination geometry, which is achieved for **2** by coordination to one Et_2timdt ligand and two bromide ions.

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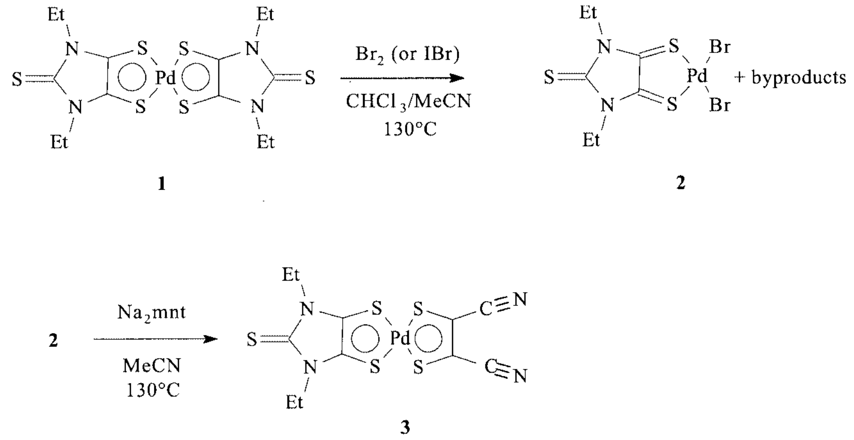


Scheme 1

The reaction of **2** with [Na$_2$mnt] (mnt = maleonitriledithiolate) in MeCN (Scheme 1) yielded dark crystals, whose X-ray crystal structure determination showed that they consist of the mixed-ligand dithiolene [Pd(Et$_2$timdt)(mnt)] (**3**; Figure 1).[15] In **3**, the C(1)−C(2) bond length within the Et$_2$timdt ligand is longer than that found in **1** [1.453(4) and 1.397(9) Å, respectively], while the C(1)−S(1) and C(2)−S(2) distances [corresponding averaged value in **1** 1.689(8) Å][7] are shorter [1.661(3) and 1.655(3) Å, respectively]. On comparing the two C$_2$S$_2$Pd metallacycles in **3**, the C−C length in the mnt unit [1.354(4) Å] is shorter than that in the Et$_2$timdt one, while the C−S distances are longer in the mnt ligand [C(3)−S(3) 1.731(3); C(4)−S(4) 1.734(3) Å]. The structural features in **1**,[7] **3**, and [Pd(mnt)$_2$], [characterised as (perylene)$_2$Pd(mnt)$_2$][16] clearly indicate that the Et$_2$timdt ligand in **3** shows a remarkable trithione character, while mnt occurs in the dithiolato form.[17]

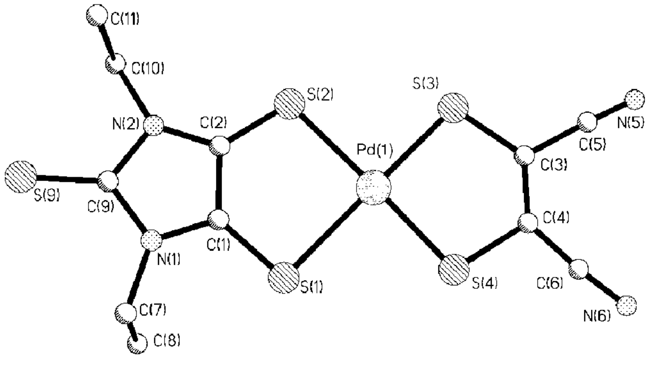
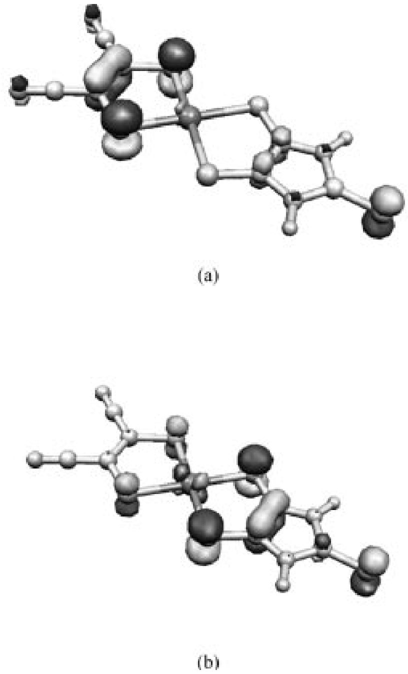


Figure 1. Molecular structure and atom labelling scheme for [Pd(Et$_2$timdt)(mnt)] (**3**); selected bond lengths (Å) and angles (°): Pd(1)−S(1) 2.3293(8), Pd(1)−S(2) 2.3300(8), Pd(1)−S(3) 2.2633(8), Pd(1)−S(4) 2.2526(8), C(1)−S(1) 1.660(3), C(2)−S(2) 1.655(3), C(3)−S(3) 1.731(3), C(4)−S(4) 1.734(3), C(1)−C(2) 1.453(4), C(3)−C(4) 1.354(4); S(1)−Pd(1)−S(2) 91.02(3), S(3)−Pd(1)−S(4) 90.59(3), S(1)−C(1)−C(2) 124.4(2), S(2)−C(2)−C(1) 124.3(2), S(3)−C(3)−C(4) 122.6(2), S(4)−C(4)−C(3) 122.1(2)

The dithiolato nature of mnt in **3** is also confirmed by its FT-Raman spectrum in the solid state: the C=C stretching vibration of the mnt unit is found at 1485 cm^{-1}, in very good agreement with the value of 1482 cm^{-1} reported for [Pd(mnt)$_2$]$^{2-}$.[18]

These experimental results are in agreement with a push-pull nature for **3**, also supported by DFT calculations carried out on the corresponding model complex [Pd(H$_2$timdt)(mnt)] (**4**). In this dithiolene, the HOMO and LUMO are π-type molecular orbitals (Figure 2): while the HOMO is mainly centred on the mnt dithiolato ligand and the terminal sulfur atom of the H$_2$timdt trithione ligand, the LUMO has a remarkable contribution from the H$_2$timdt ligand.


(a)

(b)

Figure 2. Kohn−Shan HOMO (a) and LUMO (b) calculated for [Pd(H$_2$timdt)(mnt)] (**4**)

Due to the different nature of the two ligands, a strong intramolecular polarisation can be expected for **3**, as confirmed by its remarkable solvatochromism (the position of the maximum in the NIR spectrum ranges between 920 nm in MeCN and 1060 nm in CHCl$_3$, Figure 3). On the other hand, the NBO[19] charge distribution calculated for **4** [Pd(1) 0.348, S(1,2) 0.055, S(3,4) 0.052, C(1,2) 0.016, C(3,4)

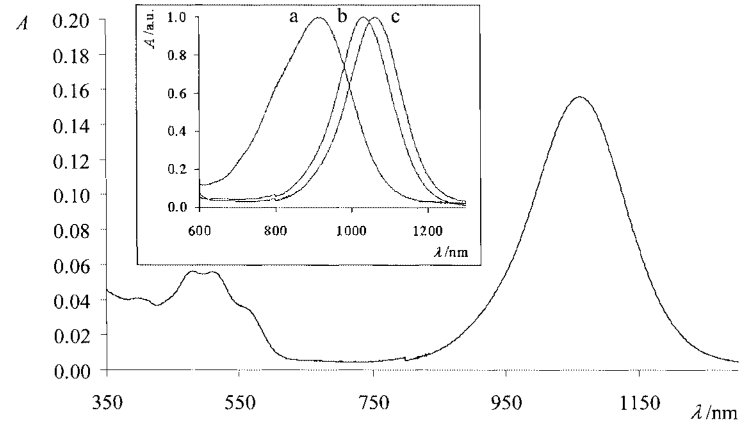


Figure 3. UV/Vis-NIR spectrum of **3** in $CHCl_3$ solution ($1.2 \cdot 10^{-5}$ M); the inset shows the superimposed normalised NIR spectra in MeCN (a), CH_2Cl_2 (b) and $CHCl_3$ (c)

−0.027, N(1,2) −0.583, C(5,6) 0.280, N(5,6) −0.271 e] agrees with a strong intramolecular polarisation. The cyclic voltammetry (Figure 4a) of complex **3** in CH_2Cl_2 shows two consecutive, (coulometrically tested) one-electron reversible reductions [$E°'_{0/-1} = +0.41$; $E°'_{-1/-2} = -0.27$ V, vs. SCE]. A one-electron irreversible oxidation (not shown in Figure 3a) is also present close to the solvent discharge ($E_{pa,\ 0/+} = +1.43$ V). On the basis of the nature of the calculated Kohn−Shan HOMO and LUMO, the reduction process should be considered as being centred mainly on the Et_2timdt ligand, while oxidation occurs mostly on the mnt unit.

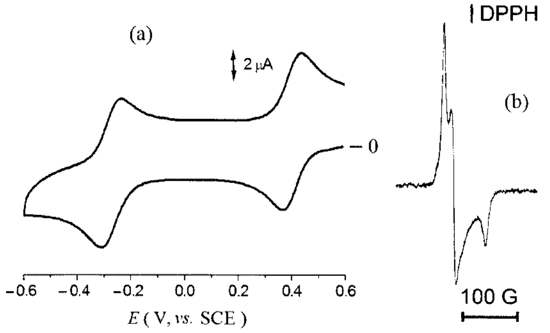


Figure 4. (a) Cyclic voltammogram recorded at a platinum electrode on a CH_2Cl_2 solution of **3** ($0.7 \cdot 10^{-3}$ M); scan rate 0.5 $V \cdot s^{-1}$; (b) X-band EPR spectrum recorded at 100 K on the electrogenerated [**3**]$^-$ monoanion

Both the monoanion and the dianion also proved to be stable over the longer time-span of macroelectrolysis. Figure 4b shows the low-temperature EPR spectrum recorded on a CH_2Cl_2 solution of the electrogenerated [Pd(Et_2timdt)(mnt)]$^{\cdot -}$ radical monoanion. The $<g>$ value of the rhombic absorption [$<g> = 1/3(g_l + g_m + g_h) = 2.013$] proved to be appreciably higher than $g_{electron}$ (2.002), confirming that the central palladium atom partly contributes to the LUMO of **3**, even though the low Δg value ($\Delta g = g_l - g_h = 0.048$) agrees with a predominantly ligand-centred reduction process.

In conclusion, by exploring the reactivity of [M(R,R′timdt)$_2$] towards Br_2 and IBr we have found an alternative method to easily prepare non-centrosymmetric push-pull [M(R,R′timdt)L] dithiolenes (L is a dithiolate ligand) with potential NLO applications.

Experimental Section

Materials and Methods: All solvents and reagents were purchased from Aldrich and used as received. The degree of purity of each compound was checked by elemental and TLC analyses. Elemental analysis, and FT-Raman, and UV/Vis-NIR spectroscopy were carried out as previously reported.[8] Cyclic voltammetry was performed in an anhydrous dichloromethane solution using electrochemical grade [NBu_4][PF_6] as supporting electrolyte in a three-electrode cell containing a platinum working electrode surrounded by a platinum-spiral counter electrode and an aqueous saturated calomel reference electrode (SCE) mounted with a Luggin capillary. A BAS 100 W electrochemical analyser was used as polarising unit. Controlled potential coulometry was performed in an H-shaped cell with anodic and cathodic compartments separated by a sintered-glass disk. The working macroelectrode was a platinum gauze; a mercury pool was used as the counter electrode. All potential values are referred to the SCE (under the present experimental conditions, the one-electron oxidation of ferrocene occurs at $E°' = +0.39$ V). X-band electron spin resonance (ESR) spectra were recorded with an ER 200 D-SRC Bruker spectrometer operating at a frequency of 9.62 GHz using a HS Bruker rectangular cavity. The operational frequency was controlled with a Hewlett−Packard x 5−32 B wavemeter and the magnetic field was calibrated with a DPPH (diphenylpicrylhydrazyl) free radical as a suitable field marker. The temperature was controlled with a Bruker ER 4111 VT device (±1 K). The g values are referred to DPPH ($g = 2.0036$) used as the external standard reference. The starting dithiolene **1** was synthesised according to the previously described method.[7]

Synthesis of [Pd(Et_2timdt)Br_2] (2): Compound **1** (50 mg, $9.2 \cdot 10^{-5}$ mol) was reacted with an excess of bromine (100 mg, $6.8 \cdot 10^{-4}$ mol) in 30 mL of a mixture of $CHCl_3$ and MeCN (1:2 v/v) for 10 minutes in an Aldrich pressure tube at 130 °C. After cooling, the precipitate was filtered off, washed with light petroleum ether, and dried under vacuum. Yield 27 mg, 60%. M.p. > 250 °C. $C_7H_{10}Br_2N_2PdS_3$ (484.6): calcd. C 17.35, H 2.08, N 5.78, S 19.85; found C 17.48, H

2.03, N 5.76, S 19.91. FT-Raman (1500−50 cm^{-1}; solid state): $\tilde{\nu}$ = 1433 (1.0), 1350 (3.5), 1300 (10.0), 1257 (3.0), 1166 (0.9), 446 (7.5), 425 (2.1) cm^{-1} (relative intensities in parentheses).

Synthesis of [Pd(Et_2timdt)(mnt)] (3): Compound **2** (31 mg, $6.3\cdot10^{-5}$ mol) was reacted with [Na_2mnt] (21 mg, $1.12\cdot10^{-4}$ mol) in 30 mL of MeCN for 30 minutes in an Aldrich pressure tube at 130 °C. After cooling, the precipitate was filtered off, washed with water, and dried under vacuum. Yield 12 mg, 40%. M.p. > 250 °C. $C_{11}H_{10}N_4PdS_5$ (464.9): calcd. C 28.42, H 2.17, N 12.05, S 34.48; found C 28.82, H 2.15, N 11.98, S 33.89. FT-Raman (1500−50 cm^{-1}; solid state): $\tilde{\nu}$ = 1485 (4.7), 1348 (5.2), 1292 (10.0), 1165 (2.7), 1059 (3.3), 530 (4.7), 449 (6.8), 362(8.7), 332 (6.7) cm^{-1} (relative intensities in parentheses).

X-ray Crystal Structure Determination: Data collections were performed on a SMART CCD area detector diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection was performed at 125 K for **2** and at room temperature for **3**. A full hemisphere of data with 0.3° steps was collected. SADABS corrections were applied. The non-hydrogen atoms were refined anisotropically except for the carbon atoms in **2** (the crystals available for **2** were very thin needles, numerous samples were examined and several types of absorption corrections performed with no improvement in the quality of the collected data or of this refinement); the calculations employed the SHELXTL program system.[20]

X-ray Structure Determination of 2: $C_7H_{10}Br_2N_2PdS_3$, monoclinic, space group $P2_1/n$, a = 13.7244(15) Å, b = 23.829(3) Å, c = 16.4013(17) Å, β = 91.404(2)°, V = 5362.3(10) $Å^3$, Z = 16, D_c = 2.401 $\mathrm{Mg/m^3}$, T = 125 K. R = 0.0525, wR = 1.004 for 7627 observed independent data.

X-ray Structure Determination of 3: $C_{11}H_{10}N_4PdS_5$, monoclinic, space group $P2_1/n$, a = 7.8685(3) Å, b = 14.0557(5) Å, c = 14.9088(6) Å, β = 90.985(1)°, V = 1648.63(11) $Å^3$, Z = 4, D_c = 1.873 $\mathrm{Mg/m^3}$, T = 293 K. R = 0.0210, wR = 0.0459 for 2364 observed independent data.

CCDC-188021 (**2**) and CCDC-188022 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Theoretical Calculations: Hybrid-DFT calculations were performed with the Gaussian 98 package[21] on compounds [Pd(H_2timdt)$_2$], [Pd(H_2timdt)Br_2], and **4**. In all cases both the Becke3LYP[22] and MPW1PW[23] hybrid functionals were used, along with the Schafer et al. basis set[24] for all atoms except Pd, for which the Hay−Wadt LANL2DZ basis set[25] with Effective Core Potentials was preferred. For each molecule, after the geometry optimisation, a normal mode frequency calculation was performed. The experimental structures are in better agreement with those calculated using the MPW1PW functional.

Supporting information: (See Footnote on the first page of this article). Optimized geometries in Cartesian coordinate form and frontier Kohn−Shan orbital energies for complexes [Pd(H_2timdt)$_2$], [Pd(H_2timdt)Br_2] and **4** are available from the authors on request.

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[15] [Ni(iPr$_2$timdt)(mnt)] — a neutral dithiolene similar to **3** — has been synthesised by the metathesis reaction between [Ni(iPr$_2$timdt)$_2$] and [Ni(mnt)$_2$]$^{2-}$ followed by oxidation of the resulting [Ni(iPr$_2$timdt)(mnt)]$^-$ with I_2, but it has not been structurally characterised: F. Bigoli, C.-T. Chen, W.-C. Wu, P. Deplano, M. L. Mercuri, M. A. Pellinghelli, L. Pilia, G. Pintus, A. Serpe, E. F. Trogu, *Chem. Commun.* **2001**, 2246−2247 and references therein.

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