Some Unsymmetrical Metal 1,2-Dithiolenes Based on Palladium, Platinum and Gold

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The unsymmetrical complexes Pd(dpedt)(dddt), Pt(dpedt)(dddt), Pd(dpedt)(dmit), and Au(dpedt)-(dddt) (where dpedt is diphenyl-ethylenedithiolate, dddt is 5,6-dihydro-1,4-dithin-2,3-dithiolate and dmit is 1,3-dithiol-2-thione-4,5-dithiolate) were prepared and characterized. The study of their chemical and electrochemical behavior showed that they are stable in air and could be candidate materials for fabrication of field-effect transistors and other devices.

Key words: Metal 1,2-Dithiolenes, Single-component Semiconductors, Electronic and Optical Devices

Introduction

During the last three decades, a number of tetrathiafulvalenes (TTFs) and metal 1,2-dithiolenes (M 1,2-DTs) have been prepared and studied (see [1 – 13] and refs. therein). Some of them have been used as channel (semiconductor) materials for field-effect transistors (FETs) [4 – 7]. Also, M 1,2-DTs have been used as nonlinear optical (NLO) [11] or photoconductive [12] materials.

Usually, the so called organic field-effect transistors (OFETs) are fabricated from a Si(n^+) gate-electrode, an SiO_2 dielectric layer, an Au source electrode, an Au drain electrode, and a channel (semiconductor) material, which consists of π-conjugate molecules or polymers [14]. During the operation of a FET, electrons or holes are injected from the source electrode to the semiconductor. Charge accumulation and transport takes place at and very close to the interface between the semiconductor and the dielectric. For p-channel (n-channel) transistors, the injection of holes (electrons) takes place when the HOMO (LUMO) level of the semiconductor aligns well with the Fermi energy level (E_F) of Au (*ca.* -4.8 to -5.1 eV). In a number of organic semiconductors (*e. g.*, TTFs), the HOMO level aligns well with the E_F of Au (p-type semiconductors), whereas the LUMO level is much higher (*ca.* -2 to -3 eV) [4, 14]. In order to inject electrons from Au electrodes (which are air-stable electrodes), the LUMO level must be lowered, increasing at the same time the stability. This is achieved by substituting some atoms or groups in the semiconductor molecules by strong electron withdrawing groups such as fluorine, cyano, or diimide moieties. A number of molecules obtained in this way showed n-type semiconductor behavior [4, 14]. For the same reason, tetracyanoquinadimethane (TCNQ) is an n-type semiconductor [4a, 4c]. Recently, it has been found that some Ni 1,2-DTs show n-type or ambipolar (both p-type and n-type) behavior [5 – 7]. Our strategy is focused on the preparation and investigation of TTFs and M 1,2-DTs stable in air, exhibiting HOMO and LUMO levels close to the E_F of Au. Taking into account the experimental data reported in [13], it is expected that the unsymmetrical Pt 1,2-DTs, Pd 1,2-DTs and Au 1,2-DTs will be stable in air as was the case with the corresponding Ni 1,2-DTs [6 – 8]. Moreover, the HOMO and LUMO levels of Pt, Pd and Au complexes could align with the E_F of Au (or other, *e. g.*, TTF-TCNQ) electrodes [4, 7, 14].

In this paper, the preparation and characterization of the unsymmetrical complexes Pd(dpedt)(dddt), Pt-(dpedt)(dddt), Pd(dpedt)(dmit), and Au(dpedt)(dddt) (where dpedt is diphenyl-ethylenedithiolate, dddt is

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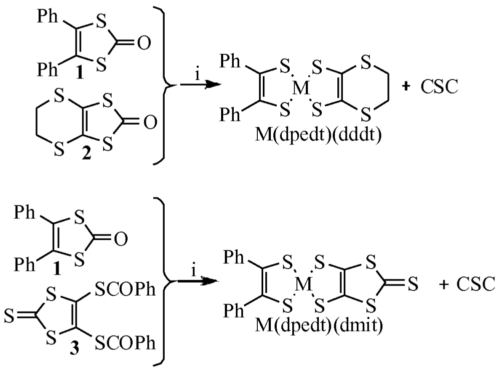

i = 1) MeONa in MeOH; 2) $PdCl_2(PhCN)_2$ in MeOH (M = Pd) or $PtCl_2(PhCN)_2$ in MeOH (M = Pt) or $NaAuCl_4$ in MeOH-H_2O (M = Au) 3) aq. HCl (35 %) in air (for M = Pd, Pt) or with Bu_4NBr_3 (for M = Au).

Scheme 1.

5,6-dihydro-1,4-dithin-2,3-dithiolate and dmit is 1,3-dithiol-2-thione-4,5-dithiolate) are described and compared to those of the Ni analogs. The new unsymmetrical complexes were prepared by the cross-coupling method [9], according to the procedure outlined in Scheme 1. The starting materials (**1**, **2**, **3**) were prepared by methods reported elsewhere (see [8, 9] and refs. therein). The required unsymmetrical complexes were separated from the corresponding symmetrical complexes (CSC) by column chromatography and characterized analytically, spectroscopically and electrochemically. For one of them, Pd(dpedt)(dddt), the crystal structure determination is reported.

Results and Discussion

From equimolar amounts of starting materials **1** and **2** or **1** and **3** and the corresponding inorganic agent, the unsymmetrical complexes Pd(dpedt)(dddt), Pt(dpedt)(dddt), Pd(dpedt)(dmit), and Au(dpedt)(dddt) were obtained in yields of 5, 0.1, 4.5 and 1 %, respectively. The success of the preparation of complexes under the strongly oxidizing conditions of Scheme 1 indicates their stability in air. The low yield in the case of the unsymmetrical complexes is due to several reasons, such as the competition with other (insoluble) byproducts [8]. The new complexes were found to be soluble in CS_2, CH_2Cl_2 and some other organic solvents. As in cases of some nickel complexes, Pt(dpedt)(dddt), Pd(dpedt)(dmit) and Au(dpedt)(dddt) can be obtained as microcrystalline or nanocrystalline precipitates from their saturated solutions in CS_2, after addition of *n*-hexane and cooling at *ca.* −10 °C. Slow crystallization from solutions gave single crystals of the complexes. However, only the crystals of Pd(dpedt)(dddt) (long needles), obtained by the solute diffusion method and using CS_2/n-hexane as solvents, were found suitable for X-ray crystal structure determination.

Table 1. Crystal data and structure refinement for Pd(dpedt)-(dddt).

Formula	$C_{18}H_{14}PdS_6$
M_r,g mol^{-1}	529.05
Crystal size, mm^3	$0.62 \times 0.12 \times 0.12$
Crystal system	orthorhombic
Space group	$Pbc2_1$
a, Å	17.6952(3)
b, Å	14.2874(2)
c, Å	7.85860(10)
V, Å^3	1986.80(5)
Z	4
D_{calcd}, g cm^{-3}	1.77
$\mu(\text{Mo}K_\alpha)$, cm^{-1}	134
$F(000)$, e	1056
hkl range	$\pm 20h$, $\pm 16k$, $-6 \le l \le 8$
$((\sin\theta)/\lambda)_{\max}$, Å^{-1}	0.583
Refl. measured	22188
Refl. unique	2982
R_{int}	0.0440
Param. refined	283
$R(F)/wR(F^2)^a$ (all refl.)	0.028/0.066
x(Flack)	0.188(9)
GoF $(F^2)^a$	1.073
$\Delta\rho_{\text{fin}}$ (max/min), e Å^{-3}	0.62/−0.37

[a] $R1 = \| F_o| - |F_c\| / \Sigma |F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c^2)^2 / \Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (0.0409P)^2 + 0.64P]^{-1}$, where $P = (\text{Max}(F_o{}^2, 0) + 2F_c{}^2)/3$, GoF $= [\Sigma w(F_o{}^2 - F_c{}^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

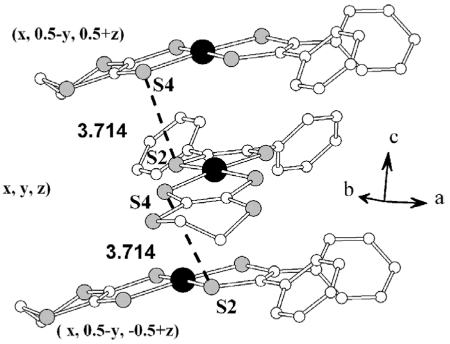

Fig. 1. Stacking of Pd(dpedt)(dddt) molecules in a column. The shortest S···S contacts are also shown.

The complex Pd(dpedt)(dddt) crystallizes in the orthorhombic system, space group $Pbc2_1$ and is isostructural with the Ni analogs, Ni(dpedt)(dddt) [8] and Ni-(dpedt)(pddt) [10]. Crystal and refinement data are summarized in Table 1.

Fig. 1 shows the stacking of Pd(dpedt)(dddt) molecules in a column along the *c* axis. In this

Table 2. Calculated E_{LUMO} and E_{HOMO} values and the corresponding electrochemical and optical absorption data.

Complex	$E_{1/2}$ (−1/0) (V)	$E^{\mathrm{rd}}_{\mathrm{onset}}$ (V)	$E^{\mathrm{ox}}_{\mathrm{onset}}$ (V)	$E^{\mathrm{opt}}_{\mathrm{onset}}$ (eV)	$E_{\mathrm{LUMO}}{}^{\alpha}$ (eV)	$E_{\mathrm{HOMO}}{}^{\alpha}$ (eV)
Ni(dpedt)(pddt)	−0.364	−0.245	0.484	0.88	−4.55	−5.28[−5.43]
Ni(dpedt)(dddt)	−0.439	−0.300	0.433	0.82	−4.51	−5.23[−5.33]
Pd(dpedt)(dddt)	−0.370	−0.239	0.397	0.92	−4.56	−5.20[−5.48]
Pt(dpedt)(dddt)	−0.345	−0.330	0.500	0.95	−4.47	−5.30[−5.42]
Ni(dpedt)(dmit)	−0.233	−0.130	0.620	0.85	−4.67	−5.42[−5.52]
Pd(dpedt)(dmit)	−0.170	−0.150	0.520	0.96	−4.65	−5.32[−5.61]
Au(dpedt)(dddt)	−0.100	−0.050	0.450	0.65	−4.75	−5.25[−5.40]

[α] The E_{LUMO} values were calculated from the reduction onset values ($-E_{\mathrm{LUMO}} = 4.8 + E^{\mathrm{rd}}_{\mathrm{onset}}$). The E_{HOMO} values were calculated from the oxidation onset values ($-E_{\mathrm{HOMO}} = 4.8 + E^{\mathrm{ox}}_{\mathrm{onset}}$). Also, E_{HOMO} values calculated from electrochemical and OA data ($E_{\mathrm{HOMO}} = E_{\mathrm{LUMO}} - E^{\mathrm{opt}}_{\mathrm{onset}}$) are given in brackets.

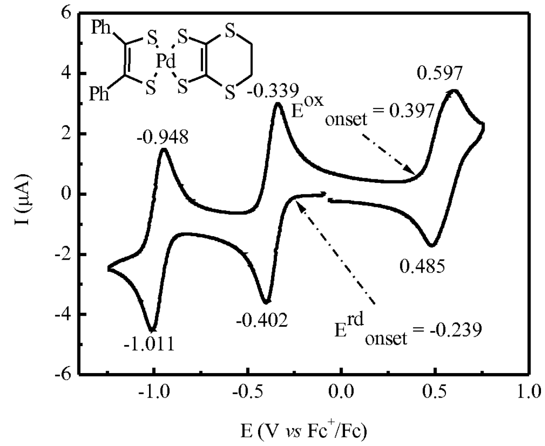

Fig. 2. Cyclic voltammogram of Pd(dpedt)(dddt) solution in CH_2Cl_2.

non-centrosymmetric structure, there is no pseudo-centrosymmetrical arrangement of metal 1,2-dithiolene molecules [13k]. The shortest S···S distance, ($S_2 \cdots S_4$) ($x, 0.5-y, 0.5+z$) = 3.714 Å, is a little larger than the sum of van der Waals radii (3.7 Å), indicating weak intermolecular interactions. The needle axis of the crystal is the *c* axis. There are two such columns per unit cell: the first one is shown in Fig. 1 and the second is generated from the first one by applying the twofold screw axis operation. This axis is parallel to the *c* axis and is passing through (0.5, 0.5, 0).

By dropping solutions of the complexes on quartz plates, followed by evaporation of the solvent and subsequent rubbing of the precipitates, thin deposits were obtained. In the case of Au(dpedt)(dddt), thin deposits were obtained easily by dropping solutions of the complex in CH_2Cl_2 and evaporation of the solvent, without rubbing. The optical absorption (OA) spectra of thin deposits of Pd(dpedt)(dddt), Pt(dpedt)(dddt), Pd(dpedt)(dmit), and Au(dpedt)(dddt) were observed at r. t. The spectra exhibit strong bands at 1038, 1037, 1022, and 1580 nm, respectively. The complexes, and especially Au(dpedt)(dddt), are optically transparent in a wide spectral range. The corresponding optical absorption onset (OA_{onset}) positions occur at 0.92, 0.95, 0.96, and 0.65 eV. The intensity and shape of the OA spectra of thin deposits remain unchanged for several months at least. This means that, in the solid state, the complexes are stable in air.

The cyclic voltammogram (CV) of each complex was recorded in CH_2Cl_2 solution containing [n-Bu_4N]PF_6 (0.5 M) and the complex (3 mM) at r. t. All potentials were referenced *versus* the ferrocenium/ferrocene (F_c^+/F_c) couple. The CV of Pd(dpedt)(dddt) is shown in Fig. 2. Similar voltammograms were obtained for the other complexes. The spectroscopic and electrochemical data of the new complexes, as well as of Ni(dpedt)(pddt), Ni(dpedt)(dddt) and Ni(dpedt)(dmit), for comparison, are listed in Table 2.

The LUMO energy level (E_{LUMO}) values were calculated from the reduction onset ($E^{\mathrm{rd}}_{\mathrm{onset}}$) values for the 1e process *via* the equation $-E_{\mathrm{LUMO}} = 4.8 + E^{\mathrm{rd}}_{\mathrm{onset}}$ [4d–6]. The HOMO energy level (E_{HOMO}) values were calculated from the oxidation onset ($E^{\mathrm{ox}}_{\mathrm{onset}}$) values for the 1e process *via* the equation $-E_{\mathrm{HOMO}} = 4.8 + E^{\mathrm{ox}}_{\mathrm{onset}}$ [4d–6]. Also, the E_{HOMO} values were calculated from electrochemical and optical absorption data *via* the equation $E_{\mathrm{HOMO}} = E_{\mathrm{LUMO}} - E^{\mathrm{opt}}_{\mathrm{onset}}$. In these cases, the optical absorption onset ($E^{\mathrm{ox}}_{\mathrm{onset}}$) values, obtained from thin deposits of complexes (rubbed samples), were used. The calculated E_{LUMO} and E_{HOMO} values are listed in Table 2, along with the electrochemical and optical data. One can see that the LUMO levels of these new materials are lower (more negative) than *ca.* −4.40 eV and the HOMO levels lower (more negative) than *ca.* −5.20 eV. These values indicate [6, 15] that the complexes are stable in air.

The described chemical, structural and physical properties indicate that the new complexes could be candidate channel materials for fabrication of n-type or ambipolar FETs, using Au or TTF-TCNQ electrodes [5, 14], as in the cases of Ni(dpedt)(dmit) [6], Ni(tmedt)(dddt) [7] and Ni(dpedt)(dddt) [7]. The position and intensity of the OA bands (see also Experimental Section) indicate that these complexes can be used as third-order nonlinear optical materials with communication wavelengths (*e. g.*, 1550 nm) [11], and/or as near-IR photoconductive materials [12]. Moreover, it is expected that the complexes with a non-centrosymmetric space group, *e. g.*, Ni(dpedt)(dddt) [8], Ni(dpedt)(pddt) [7] and Pd(dpedt)(dddt) are candidate materials for second harmonic generation [13k, 16] and similar effects [16c].

Experimental Section

(Diphenylethylenedithiolato)(5,6-dihydro-1,4-dithiin-2,3-dithiolato)palladium, Pd(dpedt)(dddt)

In a two-necked 250 mL flask, a solution-suspension of **1** (270 mg, 1 mmol) and **2** (208 mg, 1 mmol) in dry MeOH (20 mL) was prepared with stirring under nitrogen atmosphere. Then, a solution of NaOMe, freshly prepared from Na (115 mg, 5 mmol) and MeOH (10 mL), was added and the mixture stirred at r. t. for 30 min. To the obtained red solution, a solution of $PdCl_2(PhCN)_2$ (383 mg, 1 mmol) [17] in deoxygenated MeOH (80 mL) was added slowly within 15 min. The solution was stirred under nitrogen atmosphere for 1 h at r. t., whereupon the color turned brown. Then, aq. HCl (2 mL, 35 %) was added, and the mixture was transferred to a beaker and stirred in air overnight. The precipitate was filtrated, washed with water and MeOH and dried in air. The green-brown solid was extracted with CS_2 and chromatographed on silica gel, using CS_2 as eluent. The second green fraction contained Pd(dpedt)(dddt) (27 mg, 5 %). M. p. 215 °C. – UV/Vis/near IR (CS_2): $\lambda_{\max}$ ($\lg \varepsilon_{\max}$) = 980 nm (4.71). – IR (KBr): ν = 3053 (C_6H_5), 2926 (CH_2CH_2), 1378 (C=C) cm^{-1}. – $C_{18}H_{14}S_6Pd$ (527.8): calcd. C 40.86, H 2.67; found C 41.03, H 2.58.

(Diphenylethylenedithiolato)(5,6-dihydro-1,4-dithiin-2,3-dithiolato)platinum, Pt(dpedt)(dddt)

Using $PtCl_2(PhCN)_2$ (472 mg 1 mmol) [17], instead of $PdCl_2(PhCN)_2$, complex Pt(dpedt)(dddt) was obtained by the same procedure (5.5 mg, 0.1 %). M. p. 257 °C. – UV/Vis/near IR (CS_2): $\lambda_{\max}$ ($\lg \varepsilon_{\max}$) = 906 nm (4.65). – IR (KBr): ν =3053 (C_6H_5), 2923 (CH_2CH_2), 1380 (C=C) cm^{-1}. – $C_{18}H_{14}S_6Pt$ (616.9): calcd. C 35.00, H 2.28; found C 35.08, H 2.18.

(Diphenylethylenedithiolato)(5,6-dihydro-1,4-dithiin-2,3-dithiolato)gold, Au(dpedt)(dddt)

Using a solution of $NaAuCl_4 \cdot 2H_2O$ (398 mg, 1 mmol) [18] in MeOH-H_2O (10 – 0.5 mL), instead of $PdCl_2(PhCN)_2$ in MeOH, and Bu_4NBr_3 (482 mg, 1 mmol) in MeOH (30 mL), instead of aq. HCl in air, complex Au(dpedt)(dddt) was obtained by the same procedure (6.5 mg, 1 %). M. p. ≥ 235 °C (dec.). – UV/Vis/near IR (CS_2): $\lambda_{\max}$ ($lg\varepsilon_{\max}$) 1670 nm (4.66). – IR (KBr): ν = 3055 (C_6H_5), 2923 (CH_2CH_2), 1379 (C=C) cm^{-1}. – $C_{18}H_{14}S_6Au$ (616.9): calcd. C 34.89, H 2.28; found C 34.71, H 2.11.

(Diphenylethylenedithiolato)(1,3-dithiol-2-thione-4,5-dithiolato)palladium, Pd(dpedt)(dmit)

Using **1** (270 mg, 1 mmol) and **3** (409 mg, 1 mmol), instead of **1** and **2**, and applying the same procedure as for Pd(dpedt)(dddt), complex Pd(dpedt)(dmit) was obtained (24 mg, 4.5 %). M. p. ≥ 230 °C (dec.). – UV/Vis/near IR (CS_2): $\lambda_{\max}$ ($\lg \varepsilon_{\max}$) 1000 nm (4.60). – IR (KBr): ν = 3056 (C_6H_5), 1378 (C=C), 1065 (C=S) cm^{-1}. – $C_{17}H_{10}S_7Pd$ (543.8): calcd. C 37.46, H 1.85; found C 37.17, H 1.71.

X-Ray crystal structure determination

A suitable single crystal ($0.62 \times 0.12 \times 0.12$ mm^3) was mounted in an oil drop, and diffraction measurements were made under the continuous flow of nitrogen gas cooled at −93 °C, using the X-Stream 2000 (Rigaku MSC) cryogenic crystal cooler system. Measurements were performed on a Rigaku R-AXIS SPIDER image plate diffractometer using graphite-monochromated CuK_α radiation. Data collection (ω scans) and processing (cell refinement, data reduction and empirical absorption correction) were performed using the CRYSTAL CLEAR program package [19]. The structure was solved by Direct Methods using SHELXS-97 [20] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [21].

CCDC 703600 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Physical measurements

The electronic optical absorption spectra of complexes in CS_2 and/or of complexes deposited on quartz plates were recorded on a Perkin-Elmer Lamda 19 spectrometer in the range 200 – 2500 nm. Cyclic voltammetry measurements were carried out with a Bipotentiostat AFCBP1 from Pine Instrument Company fitted in a dry box and controlled with the PineChem 2.7.9 software, using a gold disk working electrode (1.6 mm diameter) and an Ag/Ag^+ (0.01 M $AgNO_3$ and 0.5 M [n-Bu_4N]PF_6 in acetonitrile) non-aqueous reference electrode (Bioanalytical Systems, Inc.) with a prolonged bridge (0.5 M [n-Bu_4N]PF_6 in acetonitrile). A thin Pt foil or gauge (8 cm^2, Sigma-Aldrich) was employed as counter electrode. The working electrode was polished using successively 6, 3, 1 mm diamond paste on a DP-Nap polishing cloth (Struers, Westlake, OH), washed with water, acetone and air-dried. The Pt foil and gauge electrodes were cleaned in a H_2O_2/H_2SO_4 (conc.) solution (1 : 4 v : v) and oven-dried. The concentration of the samples was 3 mM and that of $[n\text{-}Bu_4N]PF_6$ (supporting electrolyte) was 0.5 M. The potential sweep rate varied between 10 and 1000 mV/s. All potentials are reported *versus* the ferrocenium/ferrocene (Fc^+/Fc) couple.

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