Synthesis and Characterization of Tetrathiafulvalene (TTF) and 7,7,8,8-Tetracyanoquinodimethane (TCNQ) Compounds with PdX₂ (X = Cl, NO₃ and Hexafluoroacetylacetonate)

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Tetrathiafulvalene (TTF) reacts with $PdCl_2$, $Pd(NO_3)_2$, and $Pd(hfacac)_2$ (hfacac = hexafluoroacetylacetonate) in ethanol to give $(TTF)_{1.5}PdCl_2$ (**1a**), $(TTF)_3Pd(NO_3)_2$ (**1b**) and $(TTF)_4Pd(hfacac)_2$ (**1c**), respectively. $PdCl(TCNQ)_{2.5} \cdot CH_3OH$ (**2a**) was obtained from the reaction of $PdCl_2$ with LiTCNQ in methanol *via* the partial replacement of Cl^- in $PdCl_2$ by $TCNQ^-$ anion, whereas the total substitution of the labile NO_3^- in $Pd(NO_3)_2$ yielded $Pd(TCNQ) \cdot CH_3OH$ (**2b**). $Pd(hfacac)_2(TCNQ)_2 \cdot 3CH_3OH$ (**2c**) was obtained from $Pd(hfacac)_2$ and LiTCNQ in methanol. The prepared compounds were characterized by spectroscopic (IR, UV, XPS) methods and magnetic (EPR, magnetic susceptibility) studies. The powdered electrical conductivities (σ_{rt}) of the prepared compounds at room temperature were about $\sim 10^{-7}$ S·cm^{-1}. The effective magnetic moments were less than the spin-only value of one unpaired electron and no EPR signals from Pd metal ions were observed in any of the compounds, indicating that the Pd ions were diamagnetic and the magnetic moments arose from $(TTF)_n$ or $(TCNQ)_n$ moieties. The experimental evidences revealed that the charge transfer had occurred from $(TTF)_n$ moiety to the central Pd metal ion in **1a, 1b** and **1c**. Thus the TTF donors were partially oxidized, and the Pd metal ions were reduced from Pd(II) to Pd(0) oxidation state. The Pd metal ions in **2a** and **2b** were diamagnetic Pd(II) oxidation state. In contrast, the Pd metal ion was oxidized to Pd(IV) state in **2c** as a result of an addition of $TCNQ^-$ anion to $Pd(hfacac)_2$ in methanol. The oxidation states of the Pd metal ions were confirmed using the x-ray photoelectron spectroscopy.

Key Words : Palladium, Tetrathiafulvalene (TTF), 7,7,8,8-Tetracyanoquinodimethane (TCNQ), Charge transfer compounds

Introduction

Tetrathiafulvalene (TTF) has proven to be an excellent electron donor in the preparation of highly conductive charge transfer compounds.[1] The structural and electronic properties of TTF are considered to be important determinants of electrical-transport properties in crystals of conductive materials. It is known that 7,7,8,8-tetracyanoquinodimethane (TCNQ) can not only act as an electron acceptor, it can also bind with metals through one or more nitrile N lone pairs. Furthermore, it can coordinate to metals in different oxidation states, such as neutral, radical anionic and dianionic states.[2]

Previously, we reported on TTF or TCNQ charge transfer compounds with transition metal complexes which could be classified as novel electrical charge transfer compounds.[3] Transition metal complexes are useful in the designed synthesis of charge transfer compounds because their oxidation states are readily altered by the modification of the chemical environments around the metal ions. For example, Cu(Sp)Cl₂ [Sp = (-)-sparteine] complex, in which the copper metal ion is easily reduced from Cu(II) to Cu(I) because of the pseudo-tetrahedral geometry around the copper ion, was

used to vary the ratio of TTF in preparing $(TTF)_n CuCl_2$ charge transfer compounds.[3b]

Pd(II) complexes are of interest in this regard, since Pd(II) is readily reduced to Pd(0), and since the higher oxidation states, such as Pd(IV), are also stabilized by the appropriate ligands. In this study, we selected $PdCl_2$, $Pd(NO_3)_2$ and $Pd(hfacac)_2$ (hfacac = hexaflouroacetylacetonate) complexes, and described their reaction with TTF and TCNQ. Most TCNQ complexes may be prepared from the metathesis reaction of $TCNQ^-$ anion or the direct oxidation of appropriate metal compounds. Electrochemical synthesis has been also applied for the preparation of TCNQ complexes. In the case of the compound derived from $Pd(hfacac)_2$ and TCNQ, it is interesting to note that the resulting compound was formed by an addition of $TCNQ^-$ to the Pd(II) metal ion and the simultaneous occurrence of the oxidation from a Pd(II) to a Pd(IV) state during the reaction. The characterizations of the prepared compounds are reported in this study.

Experimental Section

Tetrathiafulvalene and 7,7,8,8-tetracyanoquinodimethane were purchased from Aldrich Chem. Co. Inc., and were used without further purification. $(TTF)_{1.5}PdCl_2$ (**1a**) was prepared from the reaction of $PdCl_2$ (0.3 mmol) and TTF (1.0

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mmol) in a mixture of deoxygenated absolute ethanol and triethylorthoformate (5 : 1 v/v). The resultant deep purple precipitates were isolated by filtration and washed several times with absolute ethanol. The microcrystalline precipitates were dried in a vacuum at room temperature. $(TTF)_3Pd(NO_3)_2$ (**1b**) was prepared from the reaction of $Pd(NO_3)_2 \cdot xH_2O$ and TTF using a similar method. $(TTF)_4Pd(hfacac)_2$ (**1c**) was obtained from $Pd(hfacac)_2$ as a TTF charge transfer compound. We also tried to prepare the compound from the reaction between TTF and $Pd(acac)_2$ (acac = acetylacetonate). but the product did not form. In the case of $(TTF)_4Pd(hfacac)_2$ it is likely that the acidity of the palladium metal ion is increased by the electronic inductive effect of the $-CF_3$ group. Therefore, $Pd(hfacac)_2$ could act as an electron acceptor when it reacts with TTF.

$PdCl(TCNQ)_{2.5} \cdot CH_3OH$ (**2a**), $Pd(TCNQ) \cdot CH_3OH$ (**2b**) and $Pd(hfacac)_2(TCNQ)_2 \cdot 3CH_3OH$ (**2c**) compounds were synthesized from the direct reaction of LiTCNQ and PdX_2 (X = Cl, NO_3 and hfacac) in CH_3OH. LiTCNQ was prepared using the literature method[4] by adding a boiling solution of LiI in acetonitrile to a boiling solution of TCNQ in acetonitrile.

Elemental analyses were performed by the Korean Basic Science Center (E.A. 1108 Elemental Analyzer). The analytical data of these compounds were given as follows: Calcd. for $(TTF)_{1.5}PdCl_2$ (**1a**). C. 22.34; H. 1.25. Found: C. 22.06; H. 1.24. Calcd. for $(TTF)_3Pd(NO_3)_2$ (**1b**). C. 25.63; H. 1.43; N. 3.32. Found: C. 24.84; H. 1.41; N. 3.05. Calcd. for $(TTF)_4Pd(hfacac)_2$ (**1c**). C. 30.52; H. 1.36. Found: C. 30.88; H. 1.28. Calcd. for $PdCl(TCNQ)_{2.5} \cdot CH_3OH$ (**2a**). C. 55.69; H. 2.15; N. 20.77. Found: C. 54.39; H. 2.05; N. 20.47. Calcd. for $Pd(TCNQ) \cdot CH_3OH$ (**2b**). C. 42.67; H. 2.11; N. 16.30. Found: C. 42.18; H. 2.34; N. 16.35. Calcd. for $Pd(hfacac)_2(TCNQ)_2 \cdot 3CH_3OH$ (**2c**). C. 43.34; H. 2.16; N. 10.93. Found: C. 43.57; H. 2.53; N. 11.64.

The powdered electrical conductivities were determined using the four-probe method. EPR spectral measurements were made on powdered samples, at room temperature and 77 K, using an ESP-300S EPR spectrometer at X-band frequency. The field modulation frequency was 100 kHz.

and DPPH was used as a reference. Magnetic susceptibility data were collected from 4 K to 300 K using the SQUID method and an MPMS7 (Magnetic Property Measurement System) from U.S.A. Quantum Design. The data were corrected for temperature independent paramagnetism and for the diamagnetism of the constituent atoms using Pascal's constants. XPS measurements were taken with an ESCALAB 220 UHV chamber of a vacuum generator using Al K_α line ($h\nu$ = 1486.6 eV) as the X-ray source. A hemispherical (CHA) analyzer about 30 cm in diameter was used as the energy analyzer. Solid IR spectra (400-4.000 cm^{-1}) were obtained using potassium bromide (KBr) pellets with a Polari's FT-IR spectrometer. Electronic absorption spectra (200-1.100 nm) were recorded on a Shimadzu 1601PC spectrophotometer in a DMF solution.

Results and Discussion

The *d.c* powdered electrical conductivities (σ_{rt}) at room temperature are given in Table 1. The powdered electrical conductivities of **1a**, **1b** and **1c** are $\sim 10^{-7}$ S·cm^{-1} which were in the insulator range. These observed conductivities indicate that the low-dimensional overlap between $(TTF)_n{}^{2-}$ units in the lattice is not expected.

The electrical conductivities of the **2b** and **2c** compounds were also $\sigma_{300K} \cong 10^{-7}$ S·cm^{-1}. These values are similar to the reported values of $M(abpt)_2(TCNQ)_2$ (M = Fe, Co, Ni and Cu) compounds.[4] in which TCNQ anions directly σ-coordinate to the central metal ions. The conductivity of the **2a** compound is in the range of being a weak semiconductor. The relatively higher conductivity of **2a** compared to **2b** and **2c** is attributed to the fact that TCNQs in **2a** were in a mixed-valence state, whereas TCNQs in **2b** and **2c** were completely ionized.[5]

The EPR spectra were obtained from the powdered samples at 77 K and at room temperature. The results are given in Table 1. The EPR spectra of **1b** and **1c** at 77 K exhibited good resolution of the anisotropic components (g_{xx}, g_{yy}, g_{zz}) with the average g values (<g>) of 2.008. These values were nearly equal to the value of the free electron or

Table 1. The room temperature electrical conductivities (σ_{rt}), EPR parameters and effective magnetic moments of the Pd compounds

Compound		σ_{rt} (Scm^{-1})	EPR parameters				$\mu_{eff}{}^b$ (BM)
			Room temperature		77 K		
			g value	$\Delta H_{pp}{}^a$	g value	ΔH_{pp}	
$(TTF)_{1.5}PdCl_2$	(**1a**)	1.66×10^{-7}	<g> = 2.0103	11	<g> = 2.0091	12	0.75
$(TTF)_3Pd(NO_3)_2$	(**1b**)	2.64×10^{-7}	g_{zz} = 2.0050 g_{yy} = 2.0100 g_{xx} = 2.0137	9	g_{zz} = 2.0031 g_{yy} = 2.0083 g_{xx} = 2.0144	11	0.81
$(TTF)_4Pd(hfacac)_2$	(**1c**)	3.11×10^{-7}	$g_{\parallel}$ = 2.0033 $g_{\perp}$ = 2.0082	9	g_{zz} = 2.0023 g_{yy} = 2.0070 g_{xx} = 2.0107	6	1.64
$PdCl(TCNQ)_{2.5} \cdot CH_3OH$	(**2a**)	4.78×10^{-6}	–	–	<g> = 2.0040	4	0.93
$Pd(TCNQ) \cdot CH_3OH$	(**2b**)	1.29×10^{-7}	–	–	<g> = 2.0037	4	0.26
$Pd(hfacac)_2(TCNQ)_2 \cdot 3CH_3OH$	(**2c**)	$< 10^{-7}$	<g> = 2.0039	10	<g> = 2.0032	10	0.95

[a]Peak to peak EPR linewidth (Gauss). [b]The effective magnetic moment were obtained by $\mu_{eff}=2.828(\chi \times T)^{1/2}$ at room temperature.
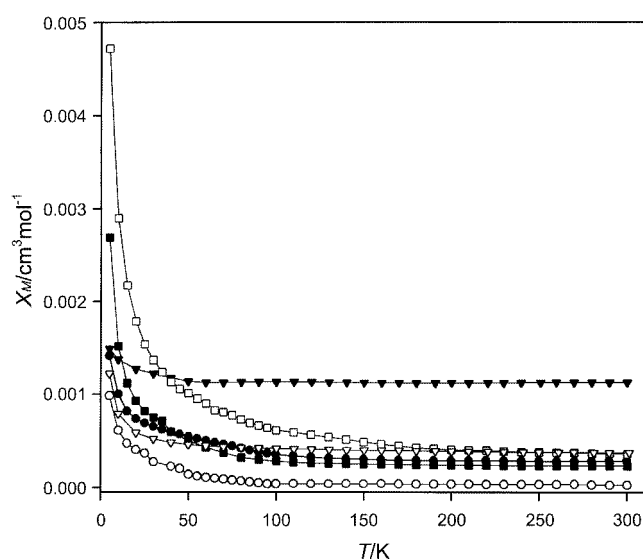
Figure 1. Temperature dependence of magnetic susceptibility for Pd compounds: ● : $(TTF)_3Pd(NO_3)_2$, ▼ : $(TTF)_4Pd(hfacac)_2$, ■ : $(TTF)_{1.5}PdCl_2$, ○ : $Pd(TCNQ)\cdot CH_3OH$, ▽ : $Pd(hfacac)_2(TCNQ)_2\cdot 3CH_3OH$ and □ : $PdCl(TCNQ)_{2.5}\cdot CH_3OH$.

the TTF cation radical in solution (g = 2.00838).[6] This indicates that the EPR signals arose from the $(TTF)_n^{2+}$ moiety. The isotropic singlet of **1a** was <g> = 2.009.

The EPR spectra of **2a** and **2c** exhibited narrow, nearly isotropic absorption at 2.003, which is associated with the TCNQ anion radical. These narrow peak-to-peak linewidths indicate that the unpaired electrons of TCNQ radicals did not couple with the metal ions.[7] No signals from the palladium metal ions were observed in any of these compounds, implying that the unpaired electrons were localized on TTF or TCNQ radicals in the prepared compounds. The diamagnetic $TCNQ^{2-}$ did not contribute to the EPR spectrum of **2b**.[8] The $TCNQ^{2-}$ anion moiety in **2b** will be shown later.

The temperature dependence of the magnetic suscepti-bilities for the prepared compounds, from 4 K to 300 K, are shown in Figure 1. The magnetic susceptibilities increase as the temperature decrease displaying a Curie-like tail. However, the data were not described by the $\chi(T) = C/T$ of the Curie law. The effective magnetic moments at 300 K were obtained using $\mu_{eff} = 2.828(\chi \times T)^{1/2}$, and the results are shown in Table 1. The effective magnetic moments (μ_{eff}) of **1a, 1b** and **1c** were 0.75-1.64 BM. These values are

somewhat less than the spin-only value of 1.73 BM for the one unpaired electron. In view of this observation and the results of the EPR spectra, we suggest that the metal ions were diamagnetic, and the unpaired electrons were localized over the $(TTF)_n^{2+}$ cation radical units. In the **2a, 2b** and **2c** compounds, the palladium metal ions were also in diamagnetic states, and the observed weak paramagnetism came from the TCNQ anion radicals.

The XPS spectra of palladium metal ions were obtained to measure the binding energy (BE) of their core electrons, and to investigate their oxidation state in the prepared compounds. The results are summarized in Table 2.

The BEs of Pd $3d_{5/2}$ in **1a, 1b** and **1c** were in the range of 336.0-337.2 eV, which were smaller than most of the other Pd(II) compounds (337.7-338.7 eV).[9,10] For example, the BE of Pd $3d_{5/2}$ in **1a** was 336.9 eV, which was smaller than that of $PdCl_2$ (338.0 eV) and $Pd(NO_3)_2$ (338.2 eV) by ~1.0 eV.[10] Comparatively, the BE values of Pd $3d_{5/2}$ in **2a** and **2b** (338.0-338.2 eV) were close to those of the other Pd(II) compounds. These observations indicate that the palladium metal ions in **1a, 1b** and **1c** are in the diamagnetic Pd(0) oxidation state resulting from a transfer of charge from the $(TTF)_n$ moiety to the palladium metal. In contrast, Pd(II) states were sustained in **2a** and **2b** during the reaction. The binding energy of Pd $3d_{5/2}$ in **2c** shifted to a higher value and was found to be 339.5 eV, implying that the oxidation state of the palladium metal ion in **2c** was higher than that of **2a** and **2b**. This observed BE is smaller than that of K_2PdCl_6 (340.2 eV),[10] but ~1.5 eV larger than that of PdO_2 (338 eV),[11] and many other Pd(II) compounds. On the basis of this result and the diamagnetic state of the palladium metal ion in **2c**, we proposed that **2c**, with the formula of $Pd^{IV}(hfacac)_2(TCNQ)_2^{2-}$, would exhibit a formal Pd(IV) oxidation state as a result of the addition of $TCNQ^{-1}$ to the $Pd(hfacac)_2$. Figure 2 shows the relation between the BEs and the oxidation states of the Pd metal ions. As the oxidation states of the Pd metal ions increased from Pd(0) → Pd(II) → Pd(IV), the 3d BEs of the palladium metal ions also increased.[12]

The BEs of the sulfur 2p core electrons in **1a, 1b** and **1c** were in the range of 163.2-163.8 eV. Each S 2p peak was slightly asymmetric with a tail at the high binding energy side, and the FWHMs were found to be 2.5 eV for **1a**, 3.1 eV for **1b**, and 2.8 eV for **1c**. Ikemoto *et al.*[13] reported that the S 2p spectra of mixed valence TTF halides, $(TTF)Br_{0.7}$ and

Table 2. The binding energies (eV) of the Pd compounds

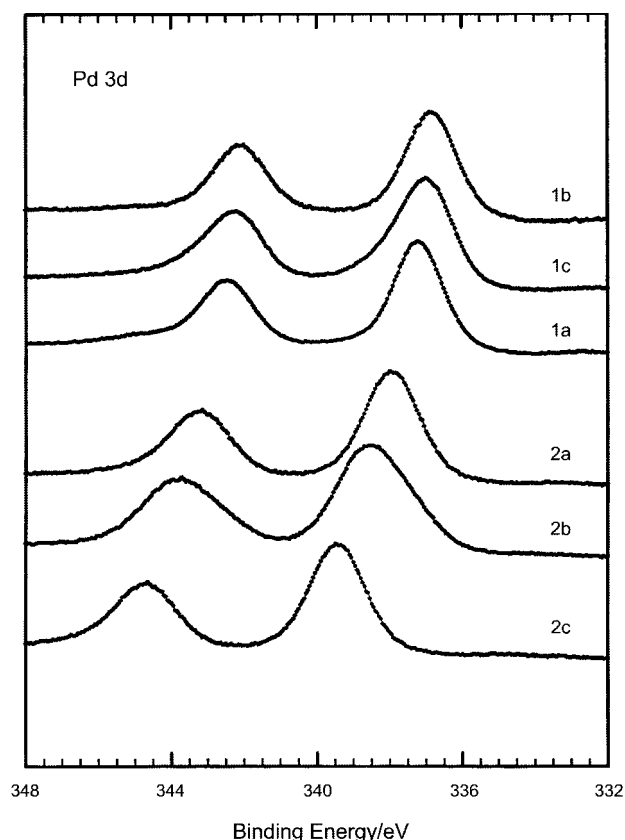| Compound	Palladium		N (1s)	S (2p) (FWHM)	Halogen
	$(3d_{5/2})$	$(3d_{3/2})$			
$(TTF)_3Pd(NO_3)_2$	336.9	342.1	401.2	163.2 (3.1 eV)	–
$(TTF)_{1.5}PdCl_2$	337.2	342.5	–	163.8 (2.5 eV)	198.1 (Cl $2p_{3/2}$)
$(TTF)_4Pd(hfacac)_2$	337.0	342.3	–	163.3 (2.8 eV)	688.0 (F 1s)
$Pd(TCNQ)\cdot CH_3OH$	338.2	343.8	399.0	–	–
$PdCl(TCNQ)_{2.5}\cdot CH_3OH$	338.0	343.2	399.2	–	198.0 (Cl $2p_{3/2}$)
$Pd(hfacac)_2(TCNQ)_2\cdot 3CH_3OH$	339.5	344.8	400.9	–	689.9 (F 1s)

Figure 2. Pd $3d_{5/2}$ and $3d_{3/2}$ binding energy spectra of the Pd compounds **1a-2c**.

$(TTF)I_{0.7}$ were significantly broader (FWHM = 2.7-3.1 eV) than those of TTF° (FWHM = 2.1 eV) and TTF^+ (FWHM = 2.5 eV). The broad linewidths were caused by the overlap of TTF° and TTF^+ components in mixed valence states. The relatively broad linewidths of S 2p peaks observed in **1a**, **1b** and **1c** (2.5-3.1 eV) provided further evidence of the mixed valence state of TTF in the $(TTF)_n^{2+}$ moiety.

The IR spectra of **1a**, **1b** and **1c** in a KBr pellet exhibited a very broad, intense band extending from 1.000-4.000 cm⁻¹, and a limited number of vibrational bands of TTF in the absorption tail. The vibrational modes were tentatively assigned by comparing their positions and intensities with the reported spectra of TTF compounds.[14] Selected spectral bands and their assignments are listed in Table 3. Of the C-C stretching bands in the five membered TTF ring, the v_{14} (v_{CC}) mode has been used to monitor the oxidation state of the TTF^{n+} cation, as it undergoes large shifts of approximately 50 cm⁻¹ per unit charge upon oxidation of TTF. The

v_{14} modes in **1b** and **1c** were observed at 1501 cm⁻¹ and 1525 cm⁻¹, respectively. These are intermediate values between a TTF molecule (1530 cm⁻¹) and a TTF^+ monocation (1478-1490 cm⁻¹),[14] which are indicative of a partially ionized TTF^δ ($0 < \delta < +1$) in **1b** and **1c**. In **1a**, the v_{14} mode shifted to a lower frequency of 1465 cm⁻¹, induced by a $(TTF)_{1.5}^{2-}$ cation, since this value is somewhat larger than those values seen in TTF^{2-} dications such as $TTF^{2-}RhCl_3$ H_2O (1450 cm⁻¹)[3a] and $TTF^{2+}(BF_3)_2$ (1440 cm⁻¹).[15]

The tentatively assigned and selected vibrational modes in **2a**, **2b** and **2c** are summarized in Table 3. The C ≡ N stretching vibrations ($v_{C\equiv N}$) in TCNQ were exhibited at 2226 and 2196 cm⁻¹, implying that **2a** contains both $TCNQ^0$ and $TCNQ^-$ anion, since the observed $v_{C\equiv N}$ values were identical to the values in $TCNQ^0$ (2226 cm⁻¹) and Li^+TCNQ^- (2197 cm⁻¹), respectively. The observation of a sharp CH bending (δ_{CH}) mode in $TCNQ^0$ at 862 cm⁻¹, in addition to the corresponding $TCNQ^-$ band at 827 cm⁻¹, also supported the suggestion that both $TCNQ^0$ and $TCNQ^-$ present in **2a**. An identical absorption phenomenon was observed and discussed in a $Cu^-(TCNQ^-)(TCNQ^0)$ compound.[16] The appearance of δ_{CH} in **2c** at 828 cm⁻¹ indicates that a $TCNQ^-$ monoanion is present in **2c**. In **2b**, the $v_{C\equiv N}$ was exhibited at 2140 cm⁻¹ which was lower than $TCNQ^0$ or $TCNQ^-$. This lower energy absorption can be explained by the addition of electron density to the C ≡ N π^* orbitals in the $TCNQ^{2-}$ dianion, indicating that **2b** can be formulated as a derivative of the $TCNQ^{2-}$ dianion.

The oxidation state of TTF and TCNQ were also examined using the electronic absorption spectra of the prepared compounds. The electronic spectra of these compounds were recorded at 200-1.100 nm in a DMF solution, and the results are in Table 3. The **1a**, **1b** and **1c** compounds showed three absorption bands. Previously, Torrance *et al.*[17] reported on the electronic spectrum of TTF^-Cl^- and assigned the three allowed transition states as 340 ($b_{3g} \rightarrow b_{1u}$), 434 ($b_{2g} \rightarrow b_{1u}$), and 581 nm ($b_{2g} \rightarrow b_{1u}$). The similarity of **1a**, **1b** and **1c** electronic spectra to that of TTF^-Cl^- implies that the TTF molecules were oxidized in **1a**, **1b** and **1c**.

Figure 3 shows the electronic spectra of **2a** and **2c** in a DMF solution. Ballester *et al.*[18] pointed out that the electronic spectrum of the TCNQ radical anion showed two locally excited transitions at about 840 and 400 nm, and that the intensity ratio, ε(840)/ε(400), would be indicative of a TCNQs electronic state. For example, the intensity ratio of 0.5 was observed in the monoanionic TCNQ, whereas the neutral TCNQ absorbs only at 840 nm. Thus, an intensity

Table 3. Selected infrared vibrational frequencies (cm⁻¹) and electronic absorption spectra of the Pd compounds

| Compound		Vibrational assignments	λ_{max} (nm) in DMF
$(TTF)_3 \cdot PdCl_2$	**(1a)**	1085 (v_{CCH}), 808 (v_{CS}), 794 ($v_{SCCring}$), 1465 (v_{CC})	305, 441, 585
$(TTF)_3 Pd(NO_3)_2$	**(1b)**	1075 (v_{CCH}), 830 (v_{CS}), 820 ($v_{SCCring}$), 1501 (v_{CC})	318, 442, 586
$(TTF)_4 Pd(hfacac)_2$	**(1c)**	1079 (v_{CCH}), 830 (v_{CS}), 820 ($v_{SCCring}$), 1525 (v_{CC})	318, 442, 586
$PdCl(TCNQ)_2 \cdot CH_3OH$	**(2a)**	2226, 2196, 2169 (v_{CN}), 1579, 1543 (s), 1508 (v_{CC}), 862, 827 (δ_{CH})	411, 422, 749, 850
$Pd(TCNQ) \cdot CH_3OH$	**(2b)**	2221, 2140 (v_{CN}), 1598, 1535 (w), 1507 (v_{CC}), 830 (δ_{CH})	341, 410, 421, 749, 850
$Pd(hfacac)_2(TCNQ)_2 \cdot 3CH_3OH$	**(2c)**	2220 (v_{CN}), 1552, 1532 (w), 1510 (v_{CC}), 828 (δ_{CH})	410, 423, 750, 850
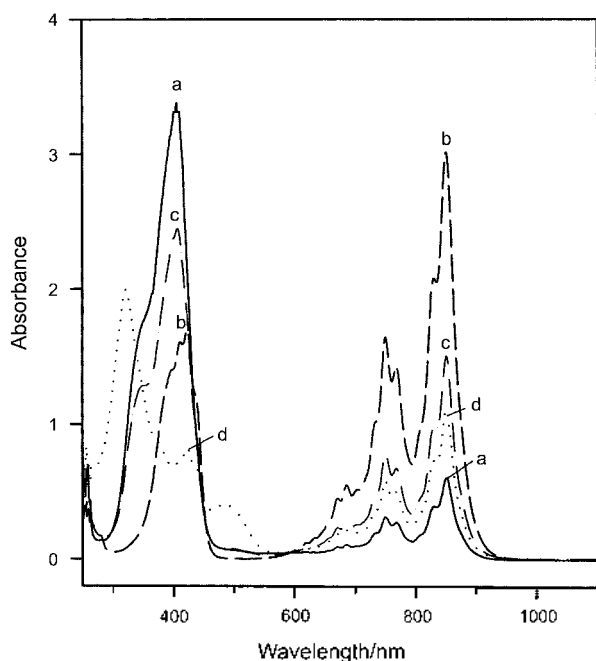
Figure 3. Electronic absorption spectra of (a) TCNQ, (b) LiTCNQ, (c) PdCl(TCNQ)₂·CH₃OH (**2a**) and (d) Pd(hfacac)₂(TCNQ)₂· 3CH₃OH (**2c**).

ratio which is higher than 0.5 would indicate the presence of both a neutral and monoanionic TCNQ. Intensity ratios of ~1.5 and ~0.5 were observed in **2a** and **2c**, respectively. We can therefore propose that both $TCNQ^0$ and $TCNQ^-$ are present in **2a** and the electronic state of the TCNQ in **2c** is -1, formulating as $(TCNQ^-)_2$. In the case of **2b**, a strong absorption peak at ~340 nm was observed, and may be associated with the $TCNQ^{2-}$ species.[19]

Conclusions

The palladium compounds were prepared using the reaction of TTF or LiTCNQ with PdX_2 (X = Cl, NO_3) and hfacac). In the $(TTF)_nPdX_2$ compounds (**1a**, **1b** and **1c**), the palladium metal ion was reduced from Pd(II) to Pd(0) by an occurrence of charge transfer from the $(TTF)_n$ moiety to the central palladium metal ion, and the TTFs were partially oxidized. The reaction of PdX_2 with LiTCNQ occurred with the partial replacement of Cl^- to give **1a**, and the substitution of the labile NO_3^- with $TCNQ^-$ yields **2b**. In the case of Pd(hfacac)₂, **2c** was formed as a result of the addition of $TCNQ^-$ to Pd(hfacac)₂, and the palladium ion was oxidized from Pd(II) to Pd(IV). To sustain the oxidative addition reaction in **2c**, Co(hfacac)₂(TCNQ)₁.₅·CH₃OH was prepared using the reaction of Co^{II}(hfacac)₂ with LiTCNQ in the same condition, as the emf value of $Co^{III} \rightarrow Co^{II}$ (1.92 V) was similar to that of $Pd^{IV} \rightarrow Pd^{II}$ (1.54 V *vs.* SHE). The oxidation state of the cobalt was investigated using the XPS spectroscopic method and magnetic property measurements.[20] It was found that the cobalt ion was also oxidized to Co^{III} during the reaction. The oxidation states of palladium

in the prepared compounds were confirmed by the XPS spectroscopic method, which is useful to ascertain the oxidation state of metal ions in palladium compounds.

Although we do not have any structural information on the prepared compounds, the metal ion in **2a**, **2b** and **2c** could be associated with the nitrogen atoms in TCNQ moiety to fulfill the coordination geometry and thus show the diamagnetic d^8 or d^6 electronic configurations. Furthermore, the low electrical conductivities of the prepared compounds indicate that the TTFs or TCNQs do not stack effectively. This suggestion should be verified using an X-ray structure determination.

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