Synthesis and Redox Property of Heterometallic (dpff)M(C_8H_4S_8) and (dpff)M(C_6S_8)M(dpff) (M = Pd and Pt, dpff = 1,1'-bis(diphenylphosphino)ferrocene)

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TTF (tetrathiafulvalene; C_8H_4S_8) has been developed as a strong electron donor in the research area of organic conductor and utilized as a building block for molecular switch, molecular magnet and supramolecular system. Electrochemically, it shows two reversible redox peaks corresponding to TTF^{0+/+1} and TTF^{+/++2} processes which can be tuned by the linkage of various functional moieties. C_8H_4S_8 is one of the versatile dithiolate-ligand derived from TTF. It has been used for the preparation of conductive metal-bisdithiolene system as well as mixed-ligand systems such as (C_8H_4S_8)M(NN) (M: Pd, Pt; (NN): pyridine-2-carboxaldehyde, 2,2'-bipyridine) and (C_8H_4S_8)M'Cp_2 (M': Ti, Zr, Hf; Cp: C_5H_5). C_6S_8 is another dithiolate-ligand derived from TTF. It has two bidentate sites and then has been utilized for a component of a bimetallic building block aiming at magnetic, electronic and optical properties.

In this paper, we report the preparation of the multi-metallic system, in which the redox active C_8H_4S_8 and C_6S_8 ligands are incorporated with Group 10 metals and ferrocenyl ligand (dpff: 1,1'-bis(diphenylphosphino)ferrocene; (C_5H_4PPh_2)_2Fe). The redox properties of these systems are also investigated by cyclic voltammetry(CV) and chemical oxidation method using a strong acceptor molecule (F4-TCNQ; tetrafluorotetracyano-p-quinodimethane).

Experimental Section

All chemicals were of reagent grade and were used without further purification. Melting points were determined using an electrothermal digital melting point apparatus IA9100 without calibration. Infrared spectra were recorded on a MIDAC FT-IR spectrophotometer, UV-Vis absorption spectra on HP 8452A diode array spectrophotometer and ^1H-NMR spectra on Bruker, Avance-500. Elemental analyses were carried out at the National Center for Inter-University Research Facilities in SNU by using CE Instrument EA1110 with CHNS-Porapack PQS column. Cyclic voltammetry was measured with an EG&G VersaStat Potentiostat/Galanostat in a methylene chloride solution (2 mL) containing 0.1 M (n-Bu)NBF_4 as electrolyte, Ag/Ag + as a reference electrode, Pt-button (0.04 cm^2), Au-button (0.04 cm^2), glassy carbon (1.0 cm^2) and ITO (0.8 cm^2) as working electrodes, Pt wire (Ø 0.3 mm) as a counter electrode and a 40 mV s^{-1} scan rate. EPR (9.79 GHz) and FAB-MS measurements were carried out at Korea Basic Science Institute in Seoul.

4,5-Bis(2'-cyanoethyldithio)-4',5'-ethylenedithio)tetrathiafulvalene (3). Compounds 1 (0.144 g, 0.5 mmol) and 2 (0.104 g, 0.5 mmol) were dissolved in freshly distilled P(OEt)_3 (4 mL) and refluxed for 1 h. The brown solution was cooled to room temperature and the dark orange precipitate was filtered, washed with methanol and dried in air. The product was then easily separated by column chromatography (SiO2, CH_2Cl_2) due to the high polarity of the cyanoethyl groups. The second orange band was collected, dried under reduced pressure and crystallized from chloroform/methanol. Yield: 78% (0.18 g). Mp: 141 °C. FT-IR (KBr, cm^-1): 2244 (C≡N), 1653, 1636, 1620 (C=C), UV (CH_2CN, nm, log ε): 222 (1.721) 256 (1.519) 312 (1.485). ^1H-NMR (CDCl_3, 500 MHz): 2.74 (t, 4H, J=7.0), 3.08 (t, 4H, J=7.0), 3.04(t, 8H, J=7.0). Compounds 6  and 2 (0.144 g, 0.5 mmol) 6  were dissolved in freshly distilled P(OEt)_3 (4 mL) and refluxed for 1 h. The brown precipitate was filtered off and washed with methylene chloride (50 mL) is added and followed by stirring for 4 h. The brown precipitate was filtered off and washed with methylene chloride. The dark brown filtrate was dried under reduced pressure and then recrystallized from methylene chloride/ethanol. For 5a: Yield: 73%. Mp: >274 °C. FT-IR (KBr, cm^-1): 1633 (C=C), 1479 (Ar C=C), 1434 (P-Ph), 824, 746, 694, 633 (Ar C-H), 546, 491 (Fe ring-tilt), 466, 436 (Fe-Cp).
UV (CH$_3$CN, nm): 200st 244sh 284m 402w 582w. For 5b: Yield: 72%. Mp: >235 $^\circ$C (dec.). EA: calc for C$_{42}$H$_{32}$S$_8$P$_2$FePt C 45.61, S 23.19, H 2.92; obsd C 45.38, S 22.77, H 2.73. FAB-MS (m/z): 1106.02 ($M^+ + 1$). FT-IR (KBr, cm$^{-1}$): 1635 (C=C), 1480 (Ar C=C), 1435 (P-Ph), 819, 770, 745, 692, 639 (Ar C-H), 554, 512, 494 (Fc ring-tilt), 471 (Fe-Cp). UV (CH$_3$CN, nm): 214st 330m 416w 554w.

Radical salts of 5b and 6b. Radical salts were prepared by mixing hot chloroform solution of 5b (or 6b) and F$_4$-TCNQ. The black powder was filtered, washed with fresh methanol, and dried in air. For (5b) · (F$_4$-TCNQ), FT-IR (KBr, cm$^{-1}$): 2192 (C≡N), 1611 (C=C), 1484 (Ar C-H), 824, 748, 693, 635 (Ar C-H), 556, 493 (Fc ring-tilt). For (6b) · (F$_4$-TCNQ), FT-IR (KBr, cm$^{-1}$): 2193 (C≡N), 1617 (C=C), 1484 (Ar C-H), 1436 (P-Ph), 824, 748, 693, 635 (Ar C-H), 556, 493 (Fc ring-tilt).

Results and Discussion

Compounds 3 and 4 were prepared by the phosphite-based coupling reaction with some modification, and obtained in higher yields (78% and 92% for 3 and 4, respectively, after chromatography purification) than the reported one (48% and 72%, respectively). These compounds were analyzed by FT-IR, UV, $^1$H-NMR and CV. This coupling reaction followed by the deprotection of four cyanoethyl groups from 4 suggests a facile way of synthesis to C$_6$S$_8$ ligand compared to the reported procedure in which an extreme condition using LDA at -78 $^\circ$C in a glovebox was applied to TTF.

Complexes 5 and 6 were synthesized by using (dppf)MCl$_2$, in which (dppf)PtCl$_2$ was prepared following the reported procedure using three-solvents system while (dppf)PdCl$_2$·CH$_2$Cl$_2$ was commercially purchased. Pd- and Pt-complexes were successfully synthesized and identified, but Ni-complexes were not clearly isolated.

Cyclic voltammograms of Pd- and Pt-complexes were measured between -0.7 V and +1.1 V by using Pt-button working electrode, the parameters of which are listed in Table 1 compared with those of 3 and 4. The CV of 5b shown in Figure 1 exhibits three reversible peaks. One peak observed at $E_{1/2}$ = -0.05 V is attributed to the redox process.
Table 1. Half-wave potentials (in volt vs Ag/Ag⁺) of the complexes

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$E_{1/2}^1$</th>
<th>$E_{1/2}^2$</th>
<th>$E_{1/2}^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.32</td>
<td>0.56</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>0.41</td>
<td>0.60</td>
<td>–</td>
</tr>
<tr>
<td>6a</td>
<td>-0.06</td>
<td>0.44</td>
<td>0.93</td>
</tr>
<tr>
<td>5b</td>
<td>-0.05</td>
<td>0.42</td>
<td>0.90</td>
</tr>
<tr>
<td>6b</td>
<td>0.09</td>
<td>0.39</td>
<td>0.87</td>
</tr>
</tbody>
</table>

*measured with Pt-button working electrode, 1 mM samples in CH₂Cl₂.

Figure 1. Cyclic voltammogram of 5b (0.1 M (n-Bu_N)BF₄ in CH₂Cl₂ with Pt-button working electrode vs. Ag/Ag⁺).

of [(dppf)Pt] moiety. The two peaks at higher potential ($E_{1/2}^1 = 0.42$ V and $E_{1/2}^1 = 0.90$ V) correspond to the redox processes of [TTF]⁻/² and [TTF]⁺¹, respectively. These potentials are compared with the reduction potential of [Cp₂Ti] moiety (-1.4 V) and the oxidation potentials of TTF moiety (0.29 V and 0.73 V; (n-Bu₄N)ClO₄ in CH₂Cl₂ vs. Ag/Ag⁺) in Cp₂Ti(C₈H₄S₈)₂. Similar redox processes are found for 6b where $E_{1/2}^1$ (0.09 V) is more anodic but $E_{1/2}^1$ (0.39 V) and $E_{1/2}^3$ (0.87 V) are more cathodic than those of 5b. It means that C₆S₈ ligand is more easily oxidized than C₈H₄S₈. The half-wave potentials of 6a measured with Pt-button working electrode (Table 1) are very close to those of 6a ($E_{1/2}^1 = -0.05$ V, $E_{1/2}^2 = 0.45$ V and $E_{1/2}^3 = 0.93$ V) measured with ITO. The half-wave potentials of 5b mentioned above are also similar to those of 5b ($E_{1/2}^1 = -0.09$ V, $E_{1/2}^2 = 0.37$ V and $E_{1/2}^3 = 0.85$ V) measured with a Au-button working electrode. The glassy-carbon working electrode, however, shows no specific redox peaks for the metal-complexes measured in this study. This can be possibly related to the rate of electron transfer. The relationship between the redox behavior of the complexes and the type of working electrode, especially for complex 5a, is now under investigation in detail.

Attempts to grow a single crystal of the radical salts with a strong acceptor F4-TCNQ were made by the electrochemical method using a typical H-type cell, but no crystals were obtained. Extended attempts by the chemical method, however, yielded the black powder which was identified as a 5b (or 6b)/F4-TCNQ complex based on FT-IR data (see Experimental Section). The N stretching frequency of neutral F4-TCNQ (2226 cm⁻¹) shifts to 2192 cm⁻¹ for the radical salts. From the frequency difference ($\Delta \omega = 34$ cm⁻¹), the degree of charge-transfer ($Z$) can be estimated as 0.77 for the two Pt-complexes from the correlation of 0.77 $\Delta \omega / Z = 44$ cm⁻¹. This is very close to that of thiophene-fuzed TTF complex of F4-TCNQ ($Z = 0.8$).

EPR spectra of the radical salts show one isotropic signal with $g = 2.004$ at room temperature which shifts to $g = 1.887$ for 5b and 1.856 for 6b at liquid N₂ temperature. The peak-to-peak line width ($\Delta H_{pp} = 12$ Gauss) is unchanged within the temperature range measured. It means that C₈H₄S₈ and C₆S₈ ligands, rather than the [(dppf)Pt] moiety, are oxidized by reaction with F4-TCNQ. This can be further confirmed by FT-IR data: (C=C) vibrational frequencies from TTF moiety in 5b (1635 cm⁻¹) and 6b (1636 cm⁻¹) shift to 1611 and 1617 cm⁻¹, respectively, in the radical salts, but those from ferrocenyl moiety (near 556 and 493 cm⁻¹) are not changed upon oxidation by F4-TCNQ.

In summary, new heterometallic complexes of (dppf)-(C₈H₄S₈)Pt(dppf) and (dppf)(C₆S₈)Pt(dppf) where M = Pd and Pt are synthesized and analyzed by elemental analysis, FAB-MS, FT-IR, UV and cyclic voltammetry. These complexes give three reversible peaks in cyclic voltammogram, among which two peaks at higher potential correspond to [TTF]⁻/² and [TTF]⁺¹, respectively, and the peak at the lowest potential to the redox process of [(dppf)M] moiety. Radical salts of (dppf)Pt(C₆S₈)Pt(dppf) and (dppf)Pt(C₈H₄S₈) with a strong acceptor F4-TCNQ are prepared by the chemical method. TTF moiety of the complexes, rather than [dppf]Pt moiety, is revealed to be oxidized by reaction with F4-TCNQ as rationalized by EPR and FT-IR data.

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References


