

Electrochromic Properties of (P2)PtL Complexes (P2 = 3,4-Dimethyl-3',4'-bis(diphenylphosphino)tetrathiafulvalene; L = 2Cl, C₆H₄S₂, C₃S₅)

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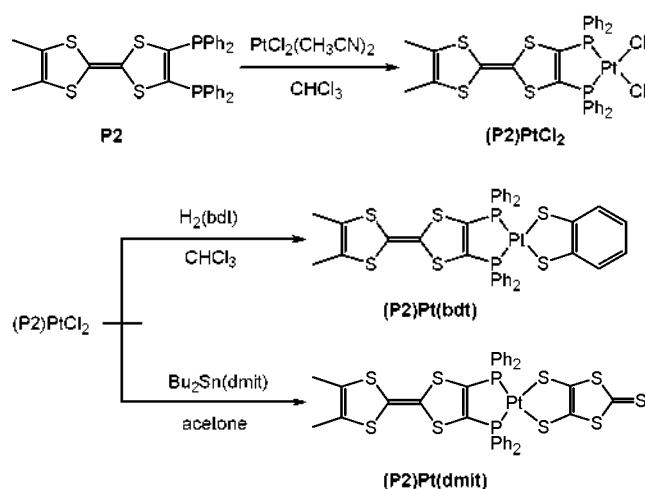
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During the last decade, heteroleptic Pt(II) complexes with P- and S-ligands have been investigated mainly focusing on their structural and electrochemical properties,¹ catalytic activity as a Pd(II) analogue,² and luminescent property.³⁻⁶ Among them, complexes with a diphosphine ligand of the π -electron rich system such as 1,1'-bis(diphenylphosphino)ferrocene (dppf) show versatile redox behaviors centered on dppf and the P₂PtS₂ core by the correlation between two heteroleptic ligands through the central metal.⁷ Very recently, we adopted a relatively new diphosphine ligand, 3,4-dimethyl-3',4'-bis(diphenylphosphino)tetrathiafulvalene (P2; Scheme 1),⁸ which is also a redox-active chelate as dppf. Using this chelate ligand, the synthesis of (P2)PtL complexes where L = 2Cl and 1,2-dithiolene, was successfully achieved. Their X-ray crystal structure analyses and redox bifunctionality were reported as well.⁹ Herein, we report the electrochromic properties of the (P2)PtL system (L = 2Cl, C₆H₄S₂ (1,2-benzenedithiolate *or* bdt) and C₃S₅ (1,3-dithiole-2-thione-4,5-dithiolate *or* dimercapto isotrithione *or* dmit) and verify the oxidation state of each phase by electronic absorption and EPR spectroscopies.

Experimental

The (P2)PtL complexes were prepared according to reported procedures (Scheme 1) and spectroscopically characterized.⁹



Scheme 1. Synthesis of (P2)PtL complexes

Electronic absorption spectra were recorded in CH₂Cl₂ on an HP 8452A diode array spectrophotometer. The X-band (9 GHz) EPR spectra of the oxidized samples generated during the bulk electrolysis (BE) experiments were recorded on a JEOL JES-TE300 EPR spectrometer using 100 kHz field modulation. The low-temperature (77 K) environment was obtained using a JEOL ES-DVT3 variable temperature controller.

Electrochemical experiments were conducted at room temperature with a CHI 620A Electrochemical Analyzer (CHI Instrument Inc.). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were measured in 1.0 mM CH₂Cl₂ solutions of the samples (4 mL) using 0.1 M *n*-Bu₄N⁺BF₄⁻ as supporting electrolyte. Ag/Ag⁻ as the reference electrode, a Pt working electrode (Pt-button with *r* = 1 mm for CV and Pt wire with 2*r* = 3.0 mm for DPV) and a Pt wire as the counter electrode with a scan rate of 50 mV s⁻¹. The bulk electrolysis (BE) experiment was performed by employing a Pt working electrode (*r* = 0.5 mm, *l* = 150 mm) and counter electrode (*r* = 0.5 mm, *l* = 10 mm) in an H-type cell in which the two compartments were separated by polyethylene film (Aldrich) and filled with a CH₃CN or 1,2-dichloroethane solution of 0.1 M *n*-Bu₄N⁺BF₄⁻ as supporting electrolyte and 1.0 mM Pt(II)-complexes.

Results and Discussion

Electrochemical Properties. The electrochemical properties of the Pt(II) complexes were investigated by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and bulk electrolysis (BE) in CH₂Cl₂ or 1,2-dichloroethane, the results of which are demonstrated in Fig. 1. Similar to the CV of TTF itself,¹⁰ P2 also showed two pairs of redox cycles with half-wave potentials of $E_{1/2}^1 = -0.096$ V and $E_{1/2}^2 = 0.432$ V, which correspond to the successive redox processes of the TTF moiety in P2, denoted as [P2]^{-/+0} and [P2]^{-2/+2}, respectively. The (P2)PtL complexes show different redox behaviors in the solution state depending upon the donor ability of the chloride and dithiolate ligands. (P2)PtCl₂ exhibits two reversible redox couples (Fig. 1 (left)) with more anodic half-wave potentials ($E_{1/2}^1 = 0.268$ V and $E_{1/2}^2 = 0.655$ V) than those of the uncoordinated P2, due to the strong electron-withdrawing property of the chloride ligand as well as the Lewis-acid character of the Pt(II) ion. On the basis of the BE results, it can be inferred that these redox cycles correspond to the two one-electron transfer processes of the TTF moiety in the coordinated P2 ligand. Furthermore, it is

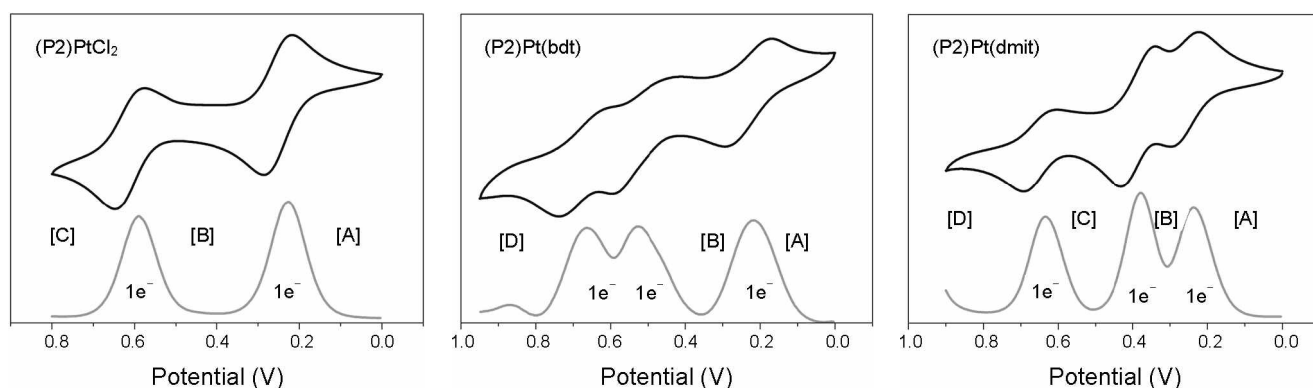


Figure 1. CV and DPV of (P2)PtL showing the BE results.

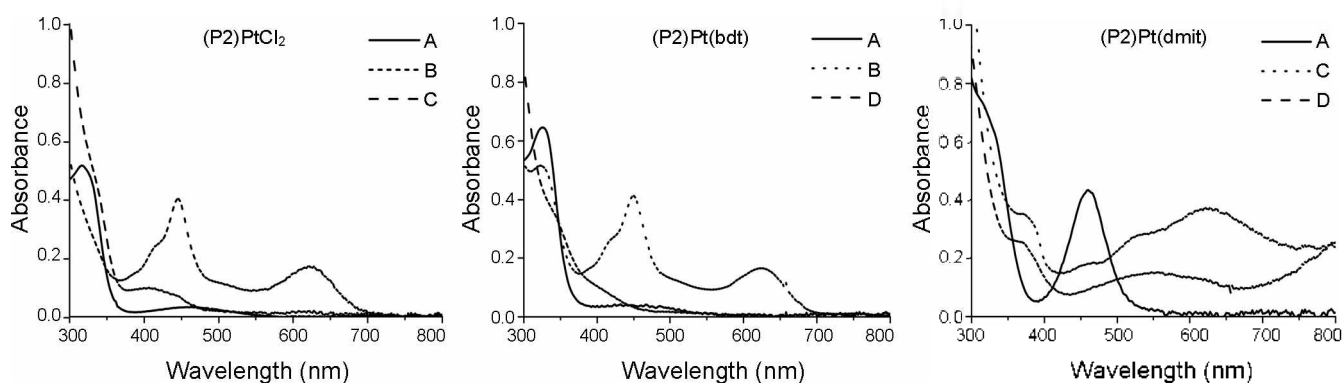


Figure 2. Electronic absorption spectra of (P2)PtL and its oxidized phases generated during the BE experiment.

noteworthy that a vivid color change of the solution occurred during the redox reactions: The orange color solution ([A]; $\lambda_{\text{max}} = 464$ nm) of the neutral complex turned into a dark green color solution ([B]; $\lambda_{\text{max}} = 624$ nm) when the first oxidation process completed, and subsequently turned into a pale yellow solution ([C]; $\lambda_{\text{max}} = 406$ nm) when the second oxidation process completed. The green color of the phase [B] is ascribed to the $[\text{TTF}]^{\cdot+}$ state, while the pale yellow color is attributed to the $[\text{TTF}]^{\cdot-}$ state of the P2 ligand.¹⁰

The (P2)Pt(dithiolate) complexes exhibit one more redox peak between the two redox peaks of the (P2)PtCl₂ complex, which can be assigned to the Pt(dithiolate)-centered redox process ($E_{1/2}^1 = 0.228$ V, $E_{1/2}^2 = 0.523$ V, $E_{1/2}^3 = 0.681$ V for (P2)Pt(bdt); $E_{1/2}^1 = 0.274$ V, $E_{1/2}^2 = 0.413$ V, $E_{1/2}^3 = 0.661$ V for (P2)Pt(dmit)). Based on the BE results, these additional redox peaks also correspond to a one-electron transfer process. Therefore, the change of the orange-colored solutions of the neutral (P2)Pt(dithiolate) complex [A] to a dark-green color ([B]; $\lambda_{\text{max}} = 624$ nm for (P2)Pt(bdt) in Fig. 1 (middle)) may have been accompanied by the formation of a radical cation on the P2 ligand, as shown in the case of (P2)PtCl₂. As regards the (P2)Pt(dmit) complex in Fig. 1 (right), a pure [B] state could not be isolated because of the overlap between the 1st and 2nd DPV peaks. However, the solution was clearly observed to turn dark green while it was being oxidized. The next oxidized state generated therefore seems to involve a bis radical cation ([C]; deep-blue color solution with $\lambda_{\text{max}} = 628$ nm). Also, on the successive oxidation of $[(\text{P2})\text{Pt}(\text{dmit})]^{2+}$, the radical cationic P2 ligand was further oxidized

to a di-cationic one with a deep-violet color ([D]) with $\lambda_{\text{max}} = 558$ nm. From these findings, it can be surmised that since the $(\text{P2})^{3+}$ species displays a pale yellow color as in the case of $[(\text{P2})\text{PtCl}_2]^{2+}$, the deep violet color of the solution is mainly due to the $[\text{Pt}(\text{dmit})]^{++}$ species in the solution. Therefore, it can be deduced that the deep blue color of the solution with the $[(\text{P2})\text{Pt}(\text{dmit})]^{2+}$ species was generated by a mixture of the dark green color of $(\text{P2})^{\cdot+}$ and the deep violet color of the $[\text{Pt}(\text{dmit})]^{++}$ species.

On the successive oxidation of $[(\text{P2})\text{Pt}(\text{bdt})]^{++}$, however, the dark green color of the phase [B] turned pale yellow immediately after two one-electron transfer processes. This suggests that the $[\text{Pt}(\text{bdt})]^{++}$ species might exhibit a pale yellow color. These electrochemical results clearly indicate that the color of the solution changes very dramatically depending on the oxidation state of the (P2)PtL complexes and the types of ligands. These vivid color changes, in turn, suggest the possibility of using these complexes in potential-dependent colorimetry.

Electronic Absorption Spectroscopy. The oxidized phases of (P2)PtL generated during the BE experiments were quenched and submitted, together with their neutral phases, to electronic absorption spectroscopy measurements at room temperature (Fig. 2) in order to verify their oxidation states.

For the neutral phase [A], a weak and broad peak due to a neutral TTF moiety appears at 464 nm for (P2)PtCl₂ and at 448 nm for (P2)Pt(bdt). But it overlaps the intense peak at 460 nm for (P2)Pt(dmit), which is attributable to the $n \rightarrow \pi^*$ transition of the C=S bond.^{7a} The mono-oxidized phase [B] of (P2)PtCl₂ and

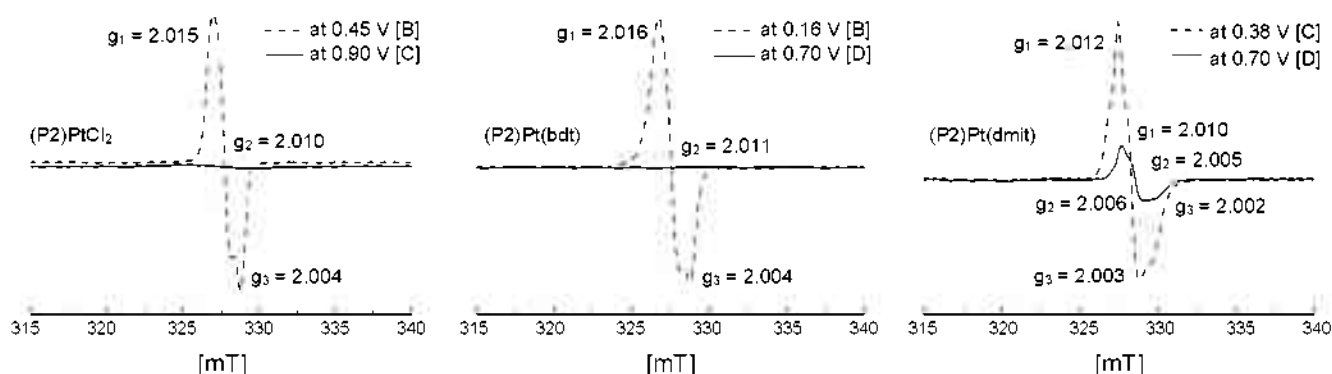


Figure 3. EPR spectra measured at 77 K for the oxidized (P2)PtL isolated at different potentials of BE experiments (1.0 mM TBABF₄ in 1,2-dichloroethane).

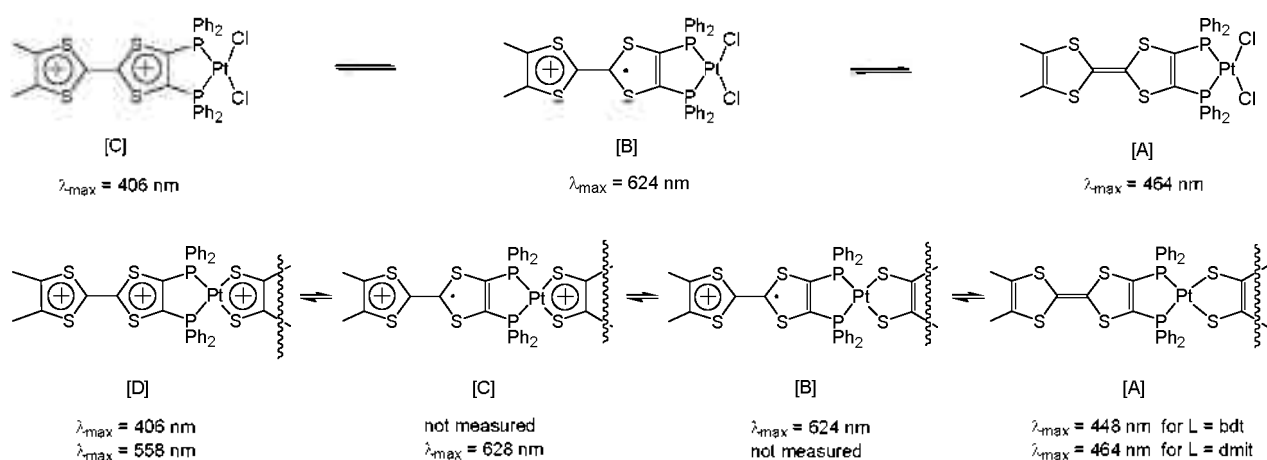


Figure 4. The proposed redox processes of (P2)PtL complexes and the absorption maxima.

(P2)Pt(bdt) shows concurrently the green color of a solution and the spectra with two intense peaks at around 450 nm and 624 nm, indicating the presence of a [TTF]^{•+} species.¹⁰ It can be rationalized from this observation that the first anodic peak in CV corresponds to the [TTF]^{•+} process rather than that of [PtL]^{•+}. Phase [C] of (P2)Pt(dmit) shows several intense and broad peaks overlapped, including that of [dmit]^{•-} at 530 nm as well as those of [TTF]^{•-} at 464 nm and 628 nm. Phase [D] of (P2)Pt(dmit) also shows more intense peaks than those of (P2)PtCl₂ and (P2)Pt(bdt). Besides [dmit]^{•-} peak at 558 nm, it shows a broad charge-transfer band over 800 nm that is not observed in the other compounds. Furthermore, the whole process of color change due to the applied potential occurs in reverse only if the species are left in air. These results suggest that (P2)Pt(dmit) carries out a more intense and contrasting color change over a potential differences than the other complexes, possibly making it as a potential electrochromic material.

EPR Spectroscopy. The oxidized (P2)PtL complexes generated during the BE experiments were quenched and submitted to EPR measurements (in 1,2-dichloroethane at 77 K) in order to verify their paramagnetic state. The radical cationic species of (P2)PtCl₂ ([B] in Fig. 1 (left)) showed a very narrow EPR signal with anisotropic g-values ($g_1 = 2.015$, $g_2 = 2.010$, $g_3 = 2.004$) as shown in Fig. 3(left). This information, combined with the electrochemical results, confirms the existence of the para-

magnetic radical cation on the P2 ligand. As regards the further oxidized species of (P2)PtCl₂ ([C] in Fig. 1 (left)), however, no EPR signal was observed at 77 K, suggesting the existence of a diamagnetic (P2)²⁺ moiety in the [(P2)PtCl₂]²⁺ species.

[(P2)Pt(bdt)]^{•+} ([B] in Fig. 1 (middle)) also shows a narrow EPR signal, very similar to that of [(P2)PtCl₂]^{•+}, with $g_1 = 2.016$, $g_2 = 2.011$ and $g_3 = 2.004$. However, the fully oxidized one ([D] in Fig. 1 (middle)) was EPR-inactive. This leads us to suggest the tri-cationic state of the complex ([(P2)Pt(bdt)]³⁺). The (P2)Pt(dmit) complex, however, shows more complicated EPR signals (Fig. 3 (right)) than those of (P2)Pt(bdt) even though they have the same heteroleptic P₂PtS₂ coordination system. The EPR signal of the deep blue solution ([C] in Fig. 1 (right)) was also anisotropic with $g_1 = 2.012$, $g_2 = 2.006$ and $g_3 = 2.003$ as shown in Fig. 3 (right). The shape of this signal suggests the presence of a mixed paramagnetic phase, possibly originating from two radical cations such as (P2)^{•+} and [Pt(dmit)]^{•+}. The deep violet colored solution of the complex ([D] in Fig. 1 (right)) exhibits an EPR signal with a lower intensity, but similar anisotropic g-values ($g_1 = 2.010$, $g_2 = 2.005$ and $g_3 = 2.002$) at 77 K. Since the doubly oxidized (P2)²⁺ species mentioned above was pale-yellow colored, it can be concluded that the deep-violet color of the solution comes from [Pt(dmit)]^{•+}. Suggested redox processes for (dppf)PtL complexes based on the combination of these interpretations are shown in Fig. 4.

Conclusion

The TTF moiety in the P2 ligand is oxidized in two steps: (P2)PtCl₂ showed $E_{1/2}^1 = 0.268$ V and $E_{1/2}^3 = 0.655$ V accompanying the color change from orange ($\lambda_{\text{max}} = 464$ nm) to pale-yellow ($\lambda_{\text{max}} = 406$ nm) via deep-green ($\lambda_{\text{max}} = 624$ nm). As for the (P2)PtL (L = bdt and dmit) complexes, one additional redox cycle ($E_{1/2}^2$) occurs in between these two potentials, corresponding to the redox process of the PtL moiety. The (P2)Pt(dmit) complex undergoes a similar color change during the redox processes from orange ($\lambda_{\text{max}} = 464$ nm) to violet ($\lambda_{\text{max}} = 558$ nm due to [Pt(dmit)]⁺) via blue ($\lambda_{\text{max}} = 628$ nm due to both (P2)⁺⁺ and [Pt(dmit)]⁺). The paramagnetic species of the complexes were confirmed by electronic absorption and EPR spectroscopies. The reversible color changes of the solution due to the applied potential imply the potential applicability of these complexes to electrochromic materials.

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