Vol. 16 高等学校化学学报 November
1995 CHEMICAL JOURNAL OF CHINESE UNIVERSITIES 241～245

Electrochemical and Spectral Studies on Ferrocene Derivatives with Electron Pushing and Drawing Substituents*

JIANG Yue-shun, YANG Wen-sheng, CHAI Xiang-dong**, ZHANG Dong
CAO Yun-wei, LI Tie-jin
(*Department of Chemistry, Jilin University, Changchun*, 130023, *P. R. China*)
Lehn Jean-marie
(*Chimie des Interactions Molèculaires, Collège de France*, 11 *Place Marcelin Berthelot*, 75005 *Paris*, *France*)

Abstract Three ferrocene derivatives, P Ⅰ: R-Fc-A, P Ⅱ: D-Fc-R and P Ⅲ: D-Fc-A (R: CH_2OH, A: $CH{=}C(CN)CONH_2$, D: $(C_{18}H_{37})_2{-}C_6H_4{-}CH{=}CH$), were studied by means of cyclic voltammetry and absorption spectroscopy. Compound P Ⅰ shows MLCT transition, P Ⅱ shows strong LMCT and P Ⅲ shows both strong LMCT and $\pi{\rightarrow}\pi^*$ CT transitions. Based on these data, frontier orbital interactions of electron pushing and drawing substituents with ferrocene group were analyzed. It was found that a drawing substituent would lower the π^* orbital energy level and a pushing substituent would raise the π orbital level.

Keywords Ferrocene derivatives, Cyclic voltammetry, Frontier orbitals, Nonlinear optical material

1 Introduction

Highly polarized organometallic compounds have been proved to be a new kind of nonlinear materials in recent years. It has been expected that such compounds with reversible centers would show different molecular hyperpolarizabilities in reduction and oxidation states, thus display an electrochemical switch behavior of spectroscopy properties[1,2]. Therefore, studies on the electrochemical and photochemical properties of these compounds become relatively important from both experimental and theoretical points of view. There have been many researches concerning the effect of pushing and drawing substituents on their electrochemical and nonlinear optical properties[3-5]. In this work, three ferrocene derivatives substituted with electron pushing and drawing groups, P Ⅰ: R—Fc—A, P Ⅱ: D—Fc—R and P Ⅲ: D—Fc—A (R: CH_2OH, A: $CH{=}C(CN)CONH_2$, D: $(C_{18}H_{37})_2{-}C_6H_4{-}CH{=}CH$),

* Supported by the National Natural Science Foundation of China.

** To whom Correspondence should be addressed.

were synthesized and the effect of the substituents on the electronic structures is analyzed based on the voltammetry and absorption spectral data from the point of frontier orbital interactions.

2 Experimental

CH_2OH—Fc—CHO was synthesized according to the reference[6]. By condensing it with 3-cyanopropanamide and [4-*N*,*N*-dioctadecylaniline]-triphenylphosphonium iodine, P Ⅰ and P Ⅱ were obtained respectively[7]. $(C_{18}H_{37})_2N-C_6H_4-CH=CH-Fc-CHO$ was prepared by oxidation of P Ⅰ with MnO_2. P Ⅱ was obtained by condensing it with 3-cyanopropanamide. All the resulting derivatives were characterized by means of microanalysis, ^1H NMR, IR and absorption spectroscopy.

The basic electrolyte for cyclic voltammetry was 0.2 mol/L TBAP in CH_2Cl_2. By using a potentiostat with incorporated sweep signal generator, the potential of the Pt spherical working electrode was scanned. Saturated calomel electrode(SCE) was used as the reference electrode to which all the potential values given in this paper were referred. The solutions were purged with Ar for 30 min before the measurements. Absorption spectra were recorded on a Shimadzu UV-365 spectrometer in CH_2Cl_2.

3 Results and Discussion

As ferrocene, P Ⅰ showed only one reversible couple with $E_{1/2}$ value of 0.63 V which is 0.24 V higher than that of ferrocene. This means the drawing-electron substituent could lower the HOMO (d_{xy}) level since CH_2OH substituent has no effect on $E_{1/2}$ of ferrocene group. The lowered HOMO level shows the interactions between LUMO(π_A^*) of the drawing substituent and $1e_{2g}$ of ferrocene group should result in bonded orbital $d_{x^2-y^2}+[\pi_A^*]$ and nonbonded orbital d_{xy}. The oxidation of P Ⅰ should occur at d_{xy} orbital. Therefore, the lowered level of d_{xy} suggests its interaction with π_A^*. The derivative with pushing-electron substituent, P Ⅱ, showed two reversible redox couples. The values of E_1^{OX} and E_2^{OX} were 0.33 and 0.59 V respectively. These results show that a pushing one raises the HOMO level of P Ⅱ since E_1^{OX} is 0.06 V lower than that of ferrocene. The HOMO should be an antibonded one, $d_{x^2-y^2}-[\pi_D]$. The second oxidation occurred at the new ligand π orbital[5], an antibonded orbital π_D-$[\Psi_{3u}]$, resulting from the interactions of π_D orbital of the pushing substituent with $1e_{1u}(\Psi_{2u}, \Psi_{3u})$ of ferrocene group. This orbital is mainly localized at π_D. The value of (E_2-E_1) for P Ⅱ is 0.26 V and this means the interval of the two ionization orbitals is 0.26 eV. Owing to the action of the strong pushing-electron substituent not only the central metal but also the ligand are oxidized more easily than that of ferrocene. The electrochemical process of P Ⅱ may be expressed as following:

$$D-Fc-R \underset{+e}{\overset{-e}{\rightleftharpoons}} D-Fc^+-R \underset{+e}{\overset{-e}{\rightleftharpoons}} D^{+\cdot}-Fc^+-R$$

The two reversible redox processes observed show that both D—Fc^+—R and $D^{+\cdot}$-Fc^+-R are stable species. $D^{+\cdot}$ should be $(C_{18}H_{37})_2N^{+\cdot}$-$C_6H_4$-CH=CH since π_D is mainly dis-

tributed at lone pair electronic orbital of $(C_{18}H_{37})_2N$: group.

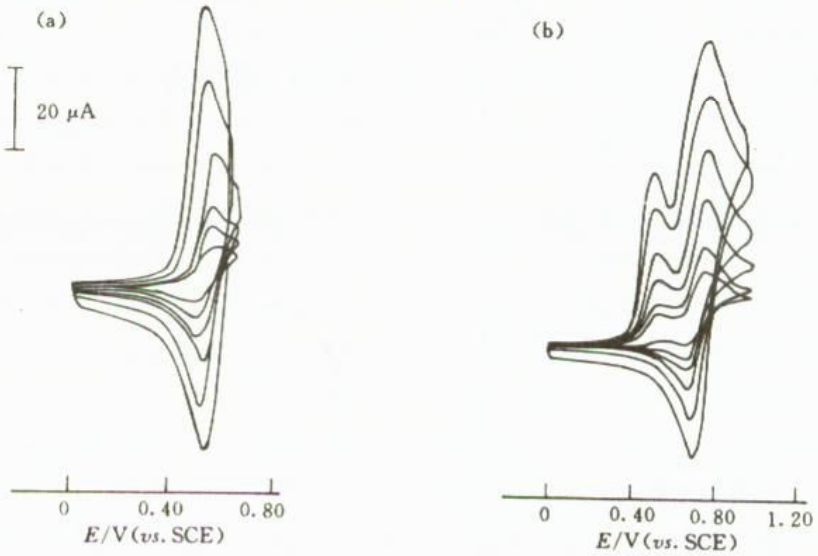


Fig. 1 Cyclic voltammograms of P Ⅱ in CH_2Cl_2 with 0.2 mol/L TBAP as supporting electrolyte recorded at scan rate of 10, 25, 50, 100, 250 and 500 mV/s (from inner circle to outer circle) respectively

a. Potential is scanned only in the range of the first couple;

b. Potential is scanned in the range of the two couples.

Fig. 1 gives the cyclic voltammograms of P Ⅱ from which two redox couples could be observed. It can be found that the first one was irreversible when potential was scanned in the range of two couples. The value of i_{pa}/i_{pc} of the second one varied with the scanning speed and reached the maximum, 1.58, at 100 mV/s. If the scanning was repeated for many times, the reduction peak of the first couple disappeared and the oxidation peak decreased rapidly. If potential was scanned only in the range of the first couple, it was a quasi-reversible process. This redox process may be expressed as:

$$D—Fc—A \underset{+e}{\overset{-e}{\rightleftharpoons}} D—Fc^+—A$$

The first couple became irreversible due to the effect of the second one when the potential was scanned in the range of the two couples. The continuous two step redox process may be expressed as:

$$D—Fc—A \xrightarrow{-e} D—Fc^+—A \underset{+e}{\overset{-e}{\rightleftharpoons}} D^{+\cdot}—Fc^+—A$$

The values of E_1^{OX} and E_2^{OX} were 0.54 and 0.73 V respectively. Compared with those from P Ⅰ and P Ⅱ, E_1^{OX} is larger than that of P Ⅱ and smaller than that of P Ⅰ. This means that there are a cumulative effect of pushing- and drawing-electron substituents on the orbital level. The value of E_1 is 0.15 V larger than that of ferrocene, this means that the interaction of $1e_{2g}$ with drawing-electron substituent is stronger than that of $1e_{2g}$ with pushing one. This strong interaction would result in very strong π backfeed effect and D(or R)—Fc—A↔D(or R)—Fc^+—A^- [3]. The bonded interaction of π_A^* with $\pi_D-[\Psi_{3u}]$ lowered the level of π_D-$[\Psi_{3u}]$ since the E_2 value of P Ⅱ is 0.14 V larger than that of P Ⅱ. The interaction of $\pi_D-[\Psi_{3u}]$with π_A^* makes $D^{+\cdot}$-Fc^+-A become unstable and the reversibility of the second

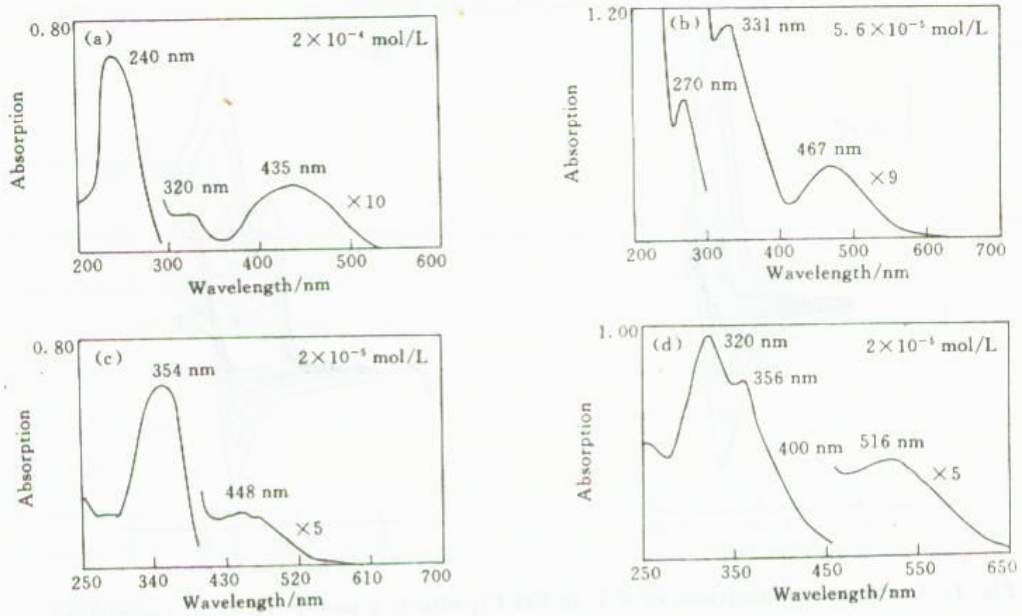
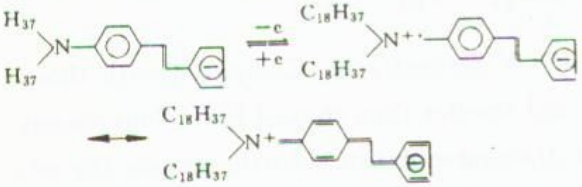


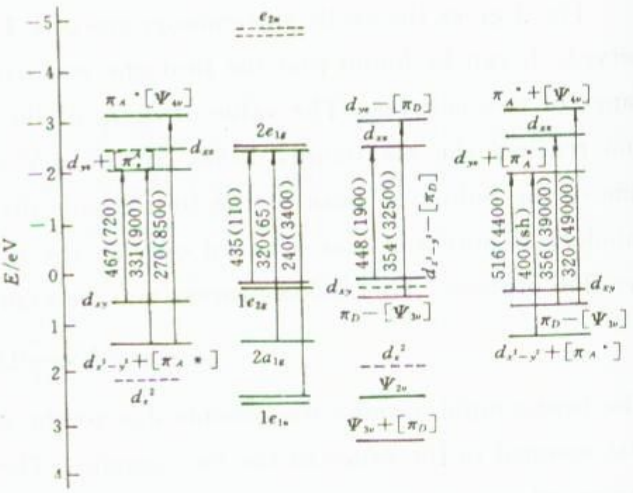
Fig. 2 UV-Visible absorption spectra of ferrocene and its deriveatives

(a) ferrocene; (b) P Ⅰ; (c) P Ⅱ; (d) P Ⅲ.

redox process is decreased. The introduction of drawing-electron substituents would strengthen the π backfeed and weaken the π coordinate effect. The two-step oxidation of metal centered and ligand π orbitals would result in the decomposition of $D^{+\cdot}—Fc^{+}—A$, therefore the first couple becomes irreversible. The second oxidation and reduction peaks still existed although $D^{+\cdot}—Fc^{+}—A$ decomposed under continuous potential scanning in the range of the two couples. This means the second reducing process should occur at $D—Cp^{-}$. This process may be expressed as following:



A stable oxidizing species was formed at this time.



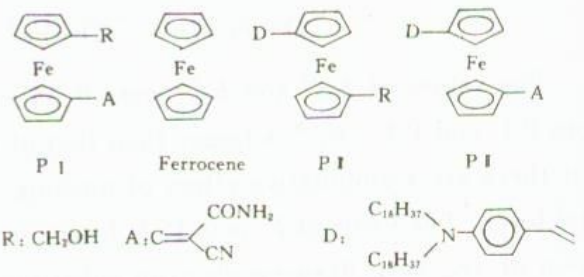


Fig. 3 A schematic diagram of orbital energy levels and spectral transitions of ferrocene and its derivatives

Molecular extinction coefficients (ε) were given in the blackets.

Fig. 2 shows the absorption spectra of ferrocene and its derivatives. Based on the electrochemical and spectral data, the orbital levels could be

given as in Fig. 3. Weak bands at 467 nm and 331 nm in spectrum of P I are assigned to the forbidden MC(Metal-Centered) transition. The strong band at 270 nm is assigned to MLCT transition. The position of this new band suggests that P I should have lowered π orbital which results from the bonded interaction of π_A^* with $e_{2u}(\Psi_{4u}, \Psi_{5u})$ of ferrocene group. Absorption spectra of P Ⅱ showed a weak band at 448 nm which is assigned to the transition from $d_{x^2-y^2}-[\pi_D]$ to d_{xz}. The strong one at 354 nm should be assigned to LMCT transition from $\pi_D-[\Psi_{3u}]$ to $d_{yz}-[\pi_D]$. The bottom level of MC transition contains ingredients of π_D, so its strongth in 19 times that of ferrocene. Owing to the π_D contained in both the top and bottom levels of LMCT transition, the LMCT band is much stronger than of ferrocene and shifts to longer wavelength. P Ⅲ contains both pushing- and drawing-electron substituents and its spectrum shows MC transition from d_{xy} to $d_{yz}+[\pi_A^*]$ at longer wavelength, 516 nm. Its ε value is larger than that of P Ⅱ because ingredients of π_A^* is contained in both top and bottom levels. The LMCT band is also stronger than that of P Ⅱ. In addition, there is a new band at 320 nm belonging to transition from $\pi_D-[\Psi_{3u}]$ to $\pi_A^*+[\Psi_{4u}]$. This band is a $\pi \longrightarrow \pi^*$ CT band which results from:

$$(C_{18}H_{37})_2N-C_6H_4-CH=CH-Fc-CH=C(CN)CONH_2 \xrightarrow{h\nu}$$

$$(C_{18}H_{37})_2N^{+\cdot}-C_6H_4-CH=CH-Fc-\dot{C}H-C^-(CN)CONH_2$$

The excited electron was transferred from pushing-electron substituent linked with top ring to the drawing one linked with the bottom ring *via* ferrocene centered metal. A completed-electron charge transfer could be realized at this time. This $\pi \longrightarrow \pi^*$ CT transition should possess larger second order susceptibility $\chi^{(2)}$ than MLCT and LMCT transitions. If a noncentrosymmetric strucutre could be constructed, for example, by LB techniques, a large SHG effect should be observed.

References

[1] Lehn J.-M., Nonlinear Optical Properties of Organic Molecules and Crystals(Ed. by Chemla D. S., Zyss J.), Academic Press, Orlando, 1987, Vol. 2, p. 215

[2] Lehn J.-M., Angew., Chem. Int. Ed. Engl., **29**: 1304(1990)

[3] Green M. L. H. *et al.*, Nature, **330**: 360(1987)

[4] Kanis D. R., Ratner M. A., Marks T. J.; Chem. Rev., **94**: 195(1994)

[5] Beer P. D.; Chem. Soc. Rev., **18**: 409(1989)

[6] Moise C. et Tirouflet J., Bulletin de la Societe Chimique de France, 1182(1969)

[7] Beer P. D., Blackburn C. Mealeer J. F., Sikanyika H.; Inorg. Chem., **29**: 378(1990)

(Received August 25, 1995)