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Voltammetric Investigation for Electron-Transfer Characteristics of Organic Semiconductors

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Two voltammertic techniques, cyclic voltammetry (CV) and chronocoulometry (CC), were employed to investigate the redox characteristics of two organic semiconductors in organic light-emitting diodes (OLED), *fac*-tris(2-phenylpyridine)iridium ($Ir(ppy)_3$) and N,N′-di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB). The electron-transfer characteristics including of oxidation formal potentials ($E^{o'}$), diffusion coefficients (D_o), electron-transfer rate constants ($k^{o'}$) were estimated by the combination of CV and CC measurements. The energy level of the highest-occupied molecular-orbital (E_{HOMO}) was also found by quantitative relationship between the oxidation potential and the ionization energy.

Keywords: *fac*-tris(2-phenylpyridine)iridium, N,N′-di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine, highest-occupied molecular-orbital, cyclic voltammetry, chronocoulometry, Anson plot, Nicholson method, quasi-reversible process, electron-transfer rate constant, diffusion coefficient, oxidation formal potentials

1. INTRODUCTION

Voltammetric analysis such as cyclic voltammetry (CV) and chronocoulometry (CC) is one of the most common analytical techniques to investigate electroactive materials [1]. Due to its versatility with inexpensiveness and ease-of-use instruments, voltammetry has been widely used in the fields of electrochemistry [2-3], inorganic/organic chemistry [3-7], material science [8-10], and biochemistry [11]. Particularly, it has become a common experiment in the study of organic electronics [12], and experienced wide usage by non-analytical chemists for the characterization of organic semiconductors.

The voltammetric techniques, however, are often misunderstood, and in some cases, the experimenter performing voltammery has a lack of the basic concepts consequently leading to scientific misconduct [13-14]. For example, some researchers have not understood that electrochemical redox reactions always correspond to the highest-occupied molecular orbital HOMO or the lowest-unoccupied molecular-orbital (LUMO) LUMO of materials. While it appears that these energy levels are easily deduced from the CV measurement, in fact, CV principally offers kinetic and mechanistic information on an electron-transfer reaction rather than thermodynamic information of the material. The electronic information should be carefully estimated from a combination of various spectroscopic measurements, with CV as only one of the complementary techniques [15-16].

Herein, we describe voltammetric analysis to determine the electron-transfer characteristics of organic semiconductors. Two of the representative compounds in organic light-emitting diodes (OLED), *fac*-tris(2-phenylpyridine)iridium (Ir(ppy)$_3$), and N,N′-Di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB), are used for the analysis (Fig. 1). They are widely known to undergo a quasi-reversible one-electron oxidation [17]. In the paper, various information including oxidation formal potential ($E^{o\prime}$), HOMO energy level (E_{HOMO}), electron-transfer rate constant ($k^{o\prime}$), and diffusion coefficient (D_o) were found solely by voltammetric analysis. Due to their quasi-reversible electrochemical oxidation, the thermodynamic and even the kinetic properties can be directly estimated from the steps of voltammetric measurements. We employed CV and CC along with the Nicholson method to analyze the compounds, and in-depth understanding of voltammetric techniques is described.

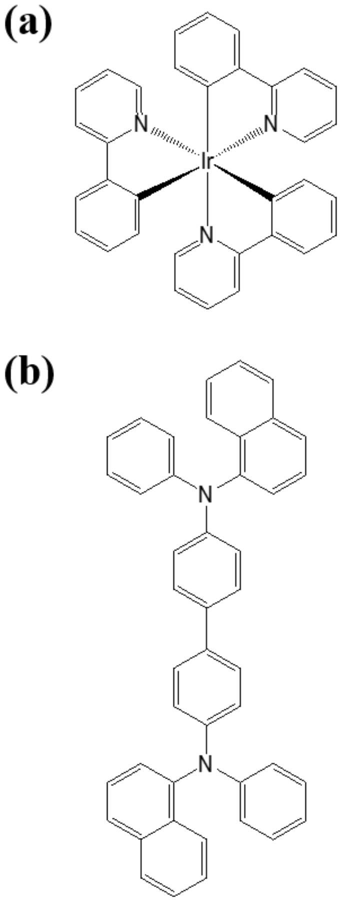

Figure 1. Chemical structure of (a) Ir(ppy)$_3$ and (b) NPB

2. EXPERIMENTAL

fac-tris(2-phenylpyridine)iridium ($Ir(ppy)_3$) and N,N′-Di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB) were purchased (Sigma-Aldrich Corp., MO, USA), and used as received. All the other reagents were purchased from either Sigma-Aldrich or TCI (Tokyo Chemical Industry, Tokyo, Japan), and used without any further purification. Electrochemical study was performed with a DY2300 Electrochemical Analyzer (Digi-Ivy, TX, USA). In the electrochemical study, cyclic voltammetry (CV) and chronocoulometry (CC) were applied to the individual solutions in order to investigate electrochemical oxidative behavior. The solutions commonly contained 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) supporting electrolyte in acetonitrile (HPLC grade) solution. Then solutions were purged with ultrapure N_2 gas before the measurement. CV was applied to platinum (2 mm dia.) electrode, and the electrochemical experiments were referenced with respect to an Ag/Ag^+ reference electrode (3 M $AgNO_3$). The working electrode was polished with 0.05 μm alumina (Buehler, IL, USA) on a felt pad following sonication in the 1:1 mixed solution of deionized water and absolute ethanol for 5 min. Then the electrode was blown by N_2 gas for 1 min.

3. RESULTS AND DISCUSSION

Firstly, the CV measurements was performed to 1.0 mM ferrocene/ferrocenium ($Fc^{0/+}$) couple in acetonitrile. The oxidation potential of Fc was determined to $E^{o\prime}(Fc^{0/+})$ = 0.089 V vs Ag/Ag^+ which was later used as an internal reference for the estimation of the HOMO level (E_{HOMO}) of the organic semiconductors. The CV was then carried out in 0.25 mM $Ir(ppy)_3$ solution, and it significantly showed quasi-reversible oxidation of $Ir(ppy)_3$ exhibiting distinctly peaked anodic and cathodic waves (Fig. 2a) for the conversion of $Ir(ppy)_3^{0/+}$ redox couple. The formal oxidation potential of $Ir(ppy)_3^{0/+}$ couple was estimated to $E^{o\prime}(Ir(ppy)_3^{0/+})$ = 0.450 V (vs Ag/Ag^+) which was placed at the average of the anodic (E_{pa}) and cathodic peak potential (E_{pc}). At the scan rate (v) of 20 mV/s, a separation of the peak potentials ($\Delta E_{pp} = E_{pa} - E_{pc}$) was observed as 78 mV of owing to the stoichiometric number of the electron transfer (one-electron) in oxidative process. The ΔE_{pp} gradually increased upon increasing v from 20 to 500 mV/s whereas $E^{o\prime}$ remained identical at 0.450 V. The ratio of anodic and cathodic peak current (i_{pa}/i_{pc}) slightly decreased from the unity when increasing v. In Fig. 2b, the i_{pa} showed directly proportional relationship to the square root of the scan rate ($v^{1/2}$) indicating heterogeneous electron transfer between the electrode and the dissolved electrochemical species under no convection ($y = 2.21\times10^{-5}\cdot x, R^2 = 0.999$).

According to Forrest *et al.* [18], the formal potential of $Ir(ppy)_3^{0/+}$ has quantitative relationship with its E_{HOMO};

$$E_{HOMO} = -(1.4 \pm 0.1)E_{CV} - (4.6 \pm 0.08)\ \text{eV} \qquad (1)$$

where E_{CV} is the relative oxidation potential of $Ir(ppy)_3^{0/+}$ calibrated with the $Fc^{0/+}$ conversion. As the E_{CV} of $Ir(ppy)_3^{0/+}$ is calculated as 0.361 V (= 0.450−0.089), the E_{HOMO} is estimated to −5.11

eV which is notably the same with that from the ultraviolet photoemission spectroscopic (UPS) measurement [18].

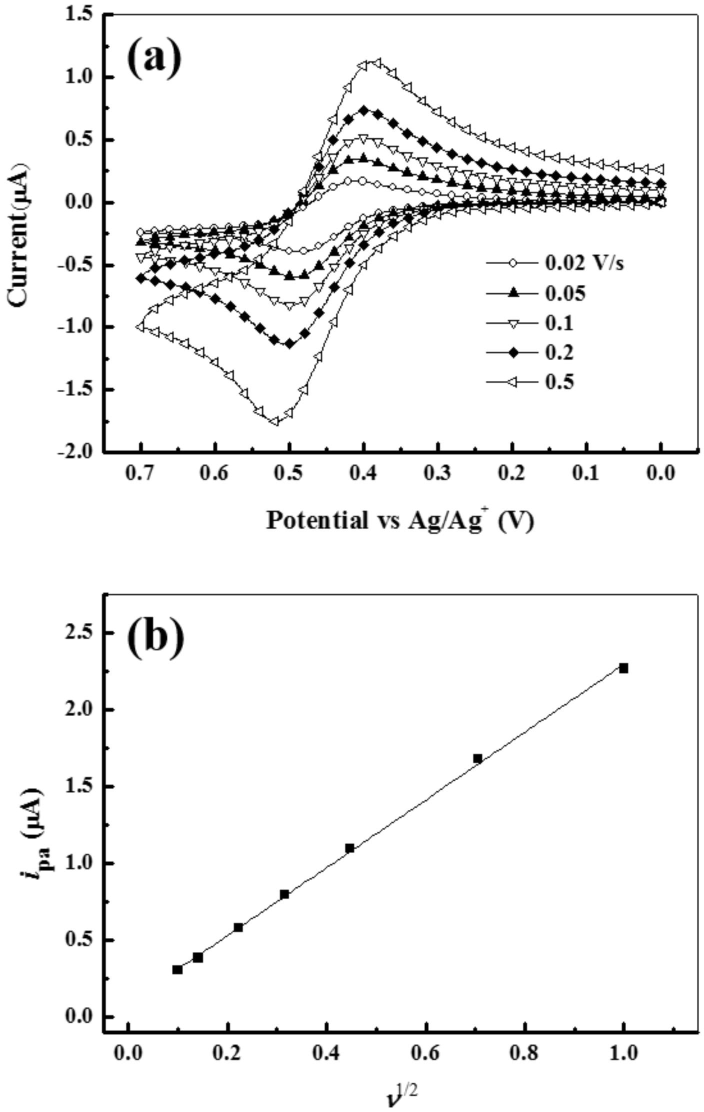

Figure 2. (a) Cyclic voltammograms of 0.25 mM $Ir(ppy)_3$, and (b) the linear increase of the anodic peak current (i_{pa}) with the square root of scan rate ($v^{1/2}$) (0.10 M TBAP, Pt working, Pt counter, and Ag/Ag$^+$ reference electrode in acetonitrile solution).

The diffusion coefficient (D_o) of $Ir(ppy)_3$ can be found by using CC measurement. In our approach, a double-step potential was applied to the solution where $Ir(ppy)_3$ was instantaneously oxidized at the vicinity of the electrode under the forward step, and then its oxidized precursor rapidly returned back to $Ir(ppy)_3$ under the step reversal. Sufficiently more positive potentials than 0.450 V were applied in the forward step (*vice versa*), and almost identical charge (Q) vs time (t) profiles were obtained when $|E_{app}-E^{o'}|$ = 0.177, 0.227, and 0.277 V (Fig. 3a). A strictly linear relationship between Q and $t^{1/2}$ ($y = 3.37\times10^{-6}\cdot x$, $R^2 = 0.999$) was obtained as Fig. 3b, and then D_o was calculated by Anson equation;

$$Q = \frac{2nFAD_o^{1/2}C^*}{\pi^{1/2}}t^{1/2} \qquad (2)$$

where n is the number of electrons, A is the actual electrode area, and C^* is the bulk concentration of Ir(ppy)$_3$.

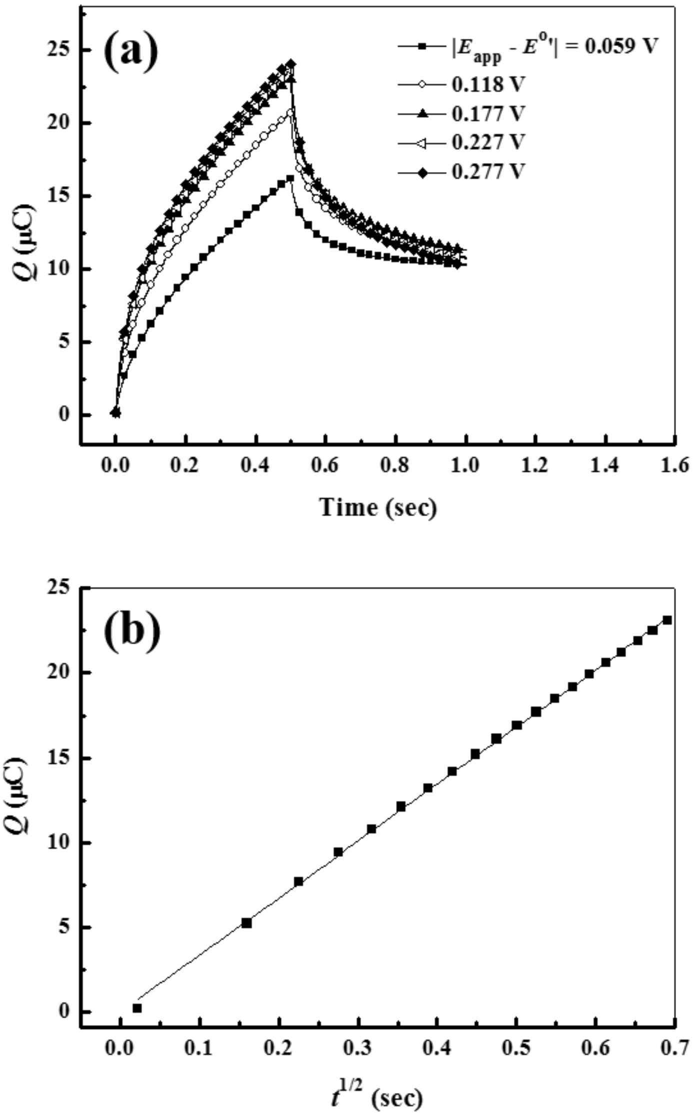

Figure 3. (a) Chronocoulomograms of 0.25 mM Ir(ppy)$_3$; two steps of potentials were applied for instantaneous oxidation of Ir(ppy)$_3$ at the first step following their reversal under the second step ($|E_{app}–E^{o\prime}|$ = 0.059, 0.118, 0.177, 0.227, 0.277 V). (b) Typical Anson correlation obtained from 0.25 mM Ir(ppy)$_3$.

As A was previously measured as 4.09×10^{-5} cm^2 using 1.0 mM Fc in acetonitrile (not shown here), the diffusion coefficient of Ir(ppy)$_3$ was, therefore, determined as $D_o = 9.20 \times 10^{-6}$ cm^2/s which is slightly higher than that of Fc in similar condition. Moreover, we finally estimated the electron-transfer rate constant ($k^{o\prime}$) of the semiconductor using the calculated D_o value. The CV data of reversible and quasi-reversible electron transfer not only offers thermodynamic information but also kinetic parameters for the redox process. Nicholson *et al.*[19] developed a diagnostics suggesting a dimensionless kinetic parameter, Ψ, which was dependent on v, D_o, and $k^{o\prime}$ of the electroactive species;

$$\Psi = \frac{k^{o\,\prime}}{[\pi D\nu(F/RT)]^{1/2}} = f(\Delta E_p) \qquad (3)$$

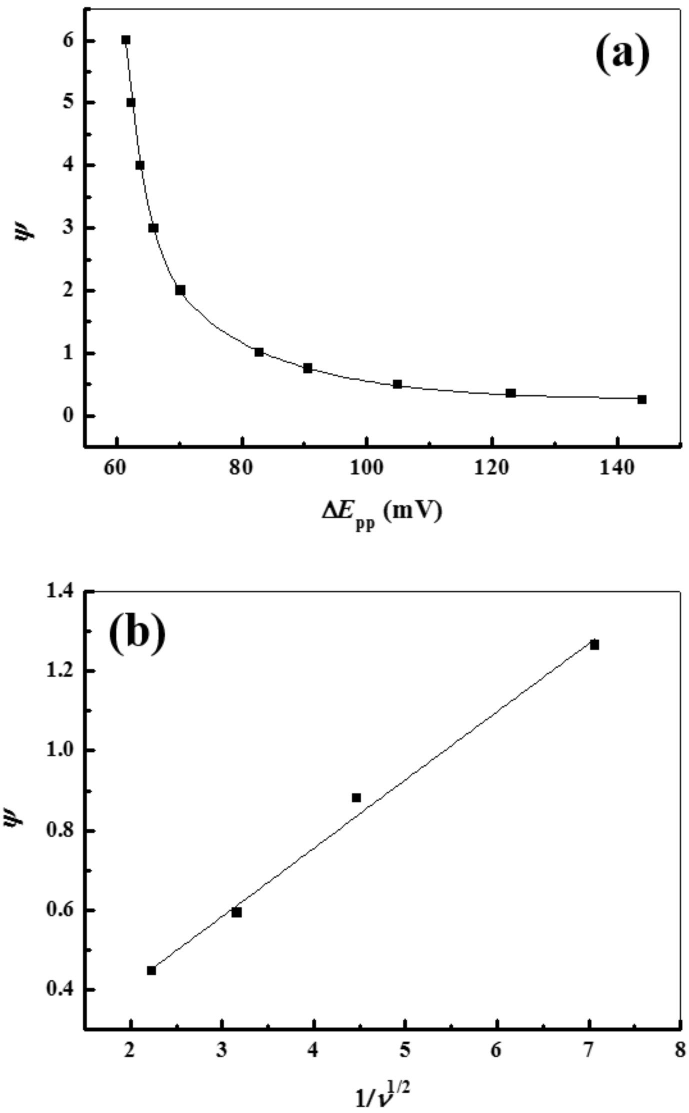

Figure 4. (a) Theoretical relationship between dimensionless kinetic parameter, Ψ and peak-to-peak potential separation (ΔE_{pp}). (b) Linear relationship between Ψ and $1/v^{1/2}$ is obtained from 0.25 mM Ir(ppy)$_3$.

Ir(ppy)$_3$ undergoes quasi-reversible one electron oxidation, which means that ΔE_{pp} is almost close to 59 mV at slow potential scan, but it increases with the scan rate under fast scan in CV measurement. According to Nicholson's method, Ψ has quantitative relationship with ΔE_{pp} (Fig. 4a). Therefore the measured value of ΔE_{pp} at various scan rates allows the determination of the value of Ψ. As shown in Fig. 4b, we extracted the Ψ values from the CVs at various potential scans, and Ψ showed a linear relationship with $1/v^{1/2}$ ($y = 1.71\times10^{-1}\cdot x$, $R^2 = 0.990$). The value of $k^{o\prime}$of Ir(ppy)$_3$ was finally calculated by the eq. (3), and determined to be 1.61×10^{-2} cm/s which was comparable with that of $Fc^{0/+}$ couple (= 1.91×10^{-2} cm/s) in similar condition [20].

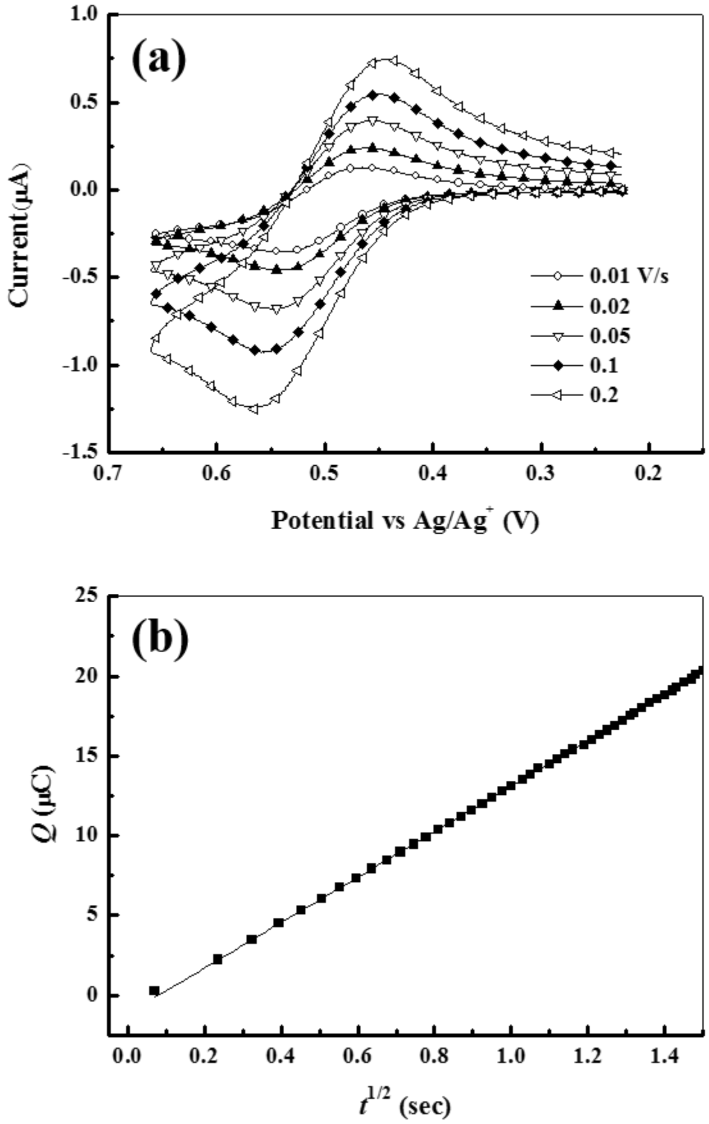

Figure 5. (a) Cyclic voltammograms and (b) Anson correlation obtained from chronocoulomogram of of 0.5 mM NPB ($|E_{\mathrm{app}}-E^{\mathrm{o}\prime}|$ = 0.177 V).

The similar procedure was performed in 0.5 mM NPB solution (0.1 M TBAP in acetonitrile). In Fig. 5a, the oxidation formal potential ($E^{\mathrm{o}\prime}$) of NPB was observed at 0.502 V vs Ag/Ag^{+} (= 0.413 V vs $Fc^{0/+}$). According to eq. (3), the E_{HOMO} of NPB was calculated as −5.18 eV and it was almost the identical to the value obtained by UPS measurement (−5.2 eV, *i.e.*) [21]. D_{o} of the NPB can also be determined using Anson plot via the CC measurement (Fig. 5b). The quasi-reversible oxidation of NPB exhibited the increase of ΔE_{pp} from the 76 to 119 mV when the scan rate v increased from 0.01 to 0.2 V/s. The dimensionless kinetic parameter, Ψ was extracted from the oxidation of NPB, and the correlation between Ψ and $1/v^{1/2}$ ($\Psi = 2.99\times10^{-1}\cdot v^{1/2}$, $R^2 = 0.999$) finally offered the $k^{\mathrm{o}\prime}$ value of NPB. The electron-transfer rate constant ($k^{\mathrm{o}\prime}$) of the NPB was then estimated to 1.05×10^{-2} cm/s.

4. CONCLUSIONS

In conclusion, two voltammertic techniques of CV and CC were presented in order to investigate the redox characteristics of organic semiconductors. Although the voltammetry is one of the most versatile analytical techniques for the study of electroactive materials, precise, appropriate understanding and experimental condition is needed. Due to the quasi-reversible oxidation characteristics of the materials, the energy level of the highest-occupied molecular-orbital (HOMO) of two representative organic semiconductors was successfully estimated by the CV measurement, and the electron-transfer kinetics including diffusion coefficients (D_o), electron-transfer rate constants ($k^{o'}$) of an organic compounds was additionally found by the combination of CV and CC measurements.

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References

1. A. J. Bard and L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications, 2nd ed., *John Wiley & Sons, New York* (2000) 226.
2. J. Heinze, *Angew. Chem. Int. Ed.*, 23 (1984) 831.
3. A. M. Abdelkader, K. T. Kilby, A. Cox and D. J. Fray, *Chem. Rev.*, 113 (2013) 2863.
4. N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, 68 (1968) 449.
5. T. C. Franklin and M. Iwunze, A*nal. Chem.*, 52 (1980) 973.
6. H. S. Lim, D. J. Barclay and F. C. Anson, *Inorg. Chem.*, 11 (1972) 1460.
7. R. J. Klingler and J. K. Kochi, *J. Am. Chem. Soc.*, 102 (1980) 4790.
8. C. M. Welch and R. G. Compton, *Anal. Bioanal. Chem.*, 396 (2010) 241.
9. R. W. Murray, *Chem. Rev.*, 108 (2008) 2688.
10. J. J. P. Roberts, J. A. Westgard , L. M. Cooper and R. W. Murray, *J. Am. Chem. Soc.*, 136 (2014) 10783.
11. C. Léger and P. Bertrand, *Chem. Rev.*, 108 (2008) 2379.
12. G. Tarabella, F. M. Mohammadi, N. Coppedè, F. Barbero, S. Iannotta, C. Santato and F. Cicoira, *Chem. Sci.*, 4 (2013) 1395.
13. F. J. Vidal-Iglesias, J. Solla-Gullon, A. Rodes, E. Herrero and A. Aldaz, *J. Chem. Edu.*, 89 (2012) 936
14. M. A. May and V. K. Gupta, *J. Chem. Edu.*, 74 (1997) 824.
15. C. L. Bentley, A. M. Bond, A. F. Hollenkamp, P. J. Mahon and J. Zhang, *Anal. Chem.*, 86 (2014) 2073.
16. L. Xiong, L. Aldous, M. C. Henstridge and R. G. Compton, *Anal. Methods*, 4 (2012) 371.
17. E.M. Gross, N.R. Armstrong and R. M. Wightman, *J. Electrochem. Soc.*, 149 (2002) E137.
18. B. W. D'Andrade, S. Datta, S. R. Forrest, P. Djurovich, E. Polikarpov and M. E. Thompson, *Org. Electron.*, 6 (2005) 11.
19. R. S. Nicholson, *Anal. Chem.*, 37 (1965) 1351.
20. The electron-transfer rate constant for the oxidation of Fc was experimentally determined using the same technique demonstrated here.

21. S. T. Lee, Y. M. Wang, X. Y. Hou and C. W. Tang, *Appl. Phys. Lett.*, 74 (1999) 670.