

Supporting Information

A Multi-Electron Transfer Ferrocene Derivative Positive Redox Moiety with Improved Solubility and Potential

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Experimental details

Synthesis process of FeCp₂PPh₂RCN

A solution of (S)-1-[(R)-2-(diphenylphosphino)ferrocenyl]ethylamine (PPFNH₂) (826 mg, 2 mmol) in 16 mL of ethanol was added 2-picolinaldehyde (214 mg, 2 mmol) and anhydrous MgSO₄ (400 mg). The reaction mixture was refluxed for 8 h, and then cooled to room temperature. The reaction mixture was diluted with 10 mL of CH₂Cl₂, and MgSO₄ were removed by filtration. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (hexanes/ethyl acetate/Et₃N, 10/1/0.1) to afford an orange solid. After recrystallized from CH₂Cl₂/*n*-hexane, ferrocenyl P,N,N-ligand (FeCp₂PPh₂RCN) was obtained as an orange solid in 85% yields. Anal. Calcd. for C₃₀H₂₇FeN₂P. C, 71.71; H, 5.38; N, 5.58. Found: C, 71.52; H, 5.36; N, 5.61. HRMS calcd. for C₃₀H₂₈FeN₂P: 503.1340, found: 503.1348.

Preparation of the electrolyte

For positive electrolyte, FeCp₂PPh₂RCN(Beijing InnoChem Science & Technology Co., Ltd)/ or ferrocene (Tianjin Da Mao chemical reagents factory) was dissolved in ethylene carbonate (EC)/propylene carbonate (PC) /ethyl methyl carbonate (EMC) (1:1:1 by volume) (LBC305-01,CAPCHEM Technology Co. Ltd) with 1 M LiPF₆ (LBC305-01, CAPCHEM Technology Co. Ltd) as the supporting electrolyte. The negative electrolyte consists of EC, PC, EMC (1:1:1 by volume) and 1 M LiPF₆ was used as the supporting electrolyte.

Cyclic voltammetry

Electrochemical measurements were carried out via an electrochemical station (Gamry reference 3000) with a three-electrode system. A glass carbon working electrode (Shanghai Chu Xi Industrial Co., Ltd.) with the diameter of 3 mm, a graphite counter electrode (2 cm×2 cm) (Jiangsu Shenzhou carbon product Co., Ltd) and a Ag/Ag⁺ reference electrodes (10 mM in MeCN) (Shanghai Huachen Instrument Co., Ltd.) were used. The cyclic voltammetry was carried out on about 20 mL electrolyte with scanning rates from 10 mV/s to 50 mV/s.

CR2032 coin-type cells assembly

The cells were assembled in an argon-filled glove box using Celgard membrane (2325, Polypore International, Inc.) as a separator with the thickness of 12 μm. The positive electrode was graphite felt (Liaoyang J-Carbon Materials Co., Ltd., China) and the negative electrode was lithium (160 μm) (Tianjin Zhongneng Lithium Industry Co., Ltd). The positive electrolyte was FeCp₂PPh₂RCN /ferrocene in (EC, DMC, EMC) (1:1:1 by volume) with 1M LiPF₆ as the supporting electrolyte. The negative electrolyte was 1M LiPF₆ in EC, DMC, EMC (1:1:1 by volume). Both the positive and negative electrolyte were 100 μL. CR2032 coin-type cells accessories were purchased from MTI Corporation.

Cyclic voltammetry (CV) curves were recorded from 2 V to 4.2 V (vs Li⁺/Li reference electrode) by an electrochemical work station (Gamry reference 3000) at 25 °C. The Cyclic voltammetry tests were measured in CR2032 coin-type cells with the graphite felt electrode as the working electrode and metallic lithium as counter and reference electrode. The resistance was measured by electrochemical impedance spectroscopy over a frequency range from 1 KHZ to 1 MHZ.

Flow battery performance

A single battery was assembled by sandwiching a polyethylene-based Celgard membrane (12 μm) (2325, Polypore International, Inc.) with a graphite felt positive electrode (Liaoyang J-Carbon Materials Co., Ltd., China), hybrid negative electrode consisted of a Li foil (160 μm) (Tianjin Zhongneng Lithium Industry Co., Ltd) and a graphite felt that were directly stacked. The above components were clamped by two bipolar plates. Two stainless end plates were used to fix all of the components. The effective size of the electrode is 9 cm² (3×3cm).

The negative electrolyte was EC,DMC,EMC (vol 1:1:1) with 1 M LiPF₆ as the supporting electrolyte, and the positive electrolyte was FeCp₂PPh₂RCN/ferrocene in 1 M LiPF₆ supporting electrolyte in EC,DMC,EMC (vol 1:1:1). About 5 mL electrolyte was pumped into the positive and negative compartment respectively. The battery test was conducted by an Arbin 2000 with current density ranging from 5 to 30 mA/cm² in the glove box at the room temperature. The charge and discharge limited voltages of a single battery with 0.1 M positive electrolyte were set as 4.3 V and 2 V for the current density of 10 mA/cm² and 20 mA/cm². For the current density of 30 mA/cm², the lower limited voltage of the discharge was set as 1.5 V considering the higher polarization. Moreover, as for the higher concentration of 0.3 M and 0.5 M, the charge and discharge limited voltages were 4.5 V and 1.5 V.

Fourier transform infrared spectra

Fourier transform infrared spectra were recorded with the positive electrolyte at different state of charge out of the positive compartment and KBr powder on an reflection fourier transformed infrared spectroscopy (JASCO FTIR 4100) at a resolution of 4 cm⁻¹ at ambient temperature. Each spectrum was recorded with the range of 4000-500 cm⁻¹ at a rate of 32 scans in transmission mode.

Electrosprayionization mass spectra

Electrosprayionization mass spectra (ESI-MS) were collected by using Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) with HESI II source in negative ion mode.

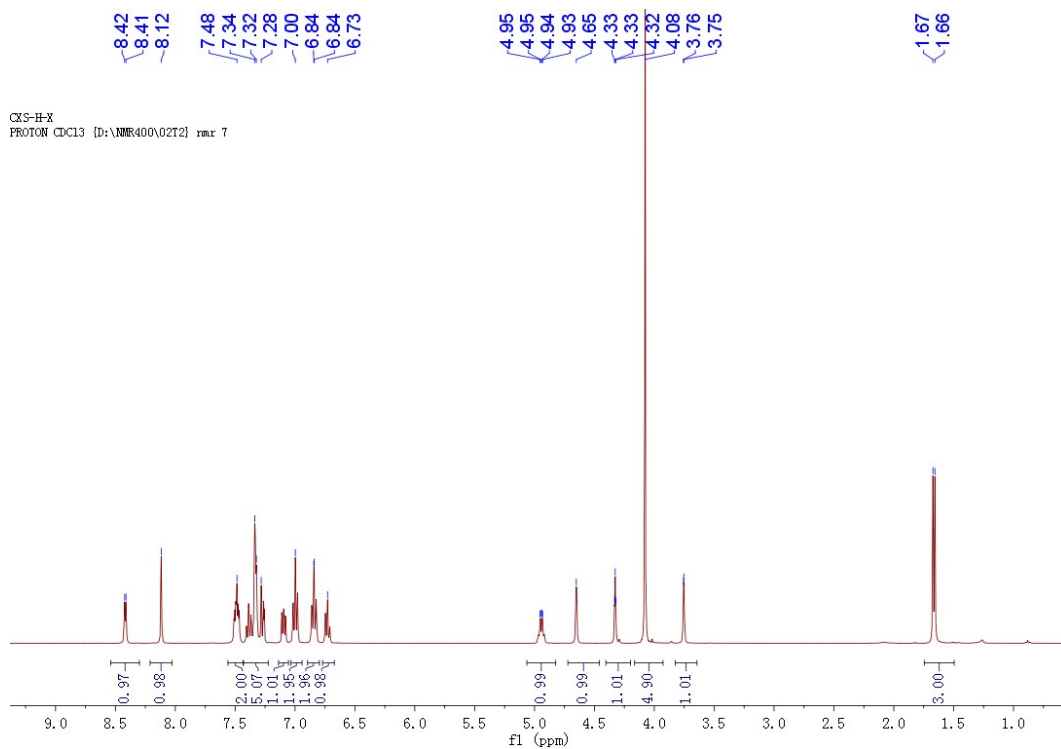


Fig. S1 ^1H NMR (400 MHz, CDCl_3) spectrum of $\text{FeCp}_2\text{PPh}_2\text{RCN}$. Major isomer: δ 8.42 (d, $J = 5.0$ Hz, 1H), 8.12 (s, 1H), 7.48-7.28 (m, 7H), 7.12 (t, 1H), 7.00 (t, 2H), 6.84 (t, 2H), 6.73 (t, 1H), 4.94 (q, $J=8.0$ Hz, 1H), 4.66 (s, 1H), 4.33 (s, 1H), 4.08 (s, 5H), 3.76 (s, 1H), 1.67 (d, $J = 8.0$ Hz, 3H).

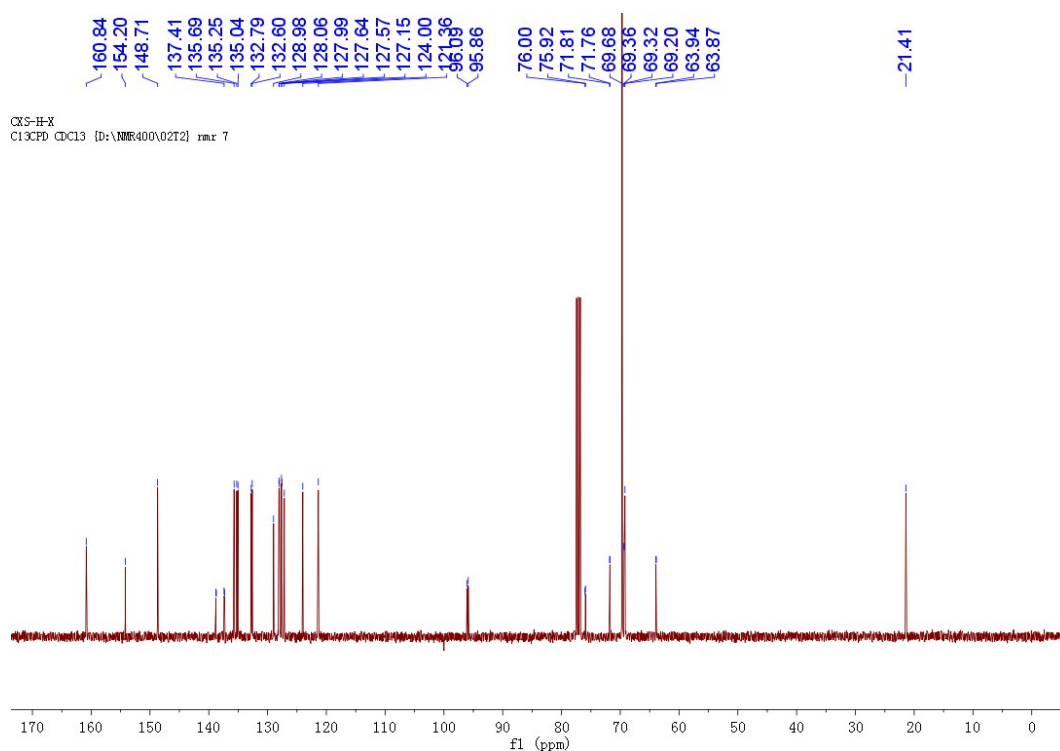


Fig. S2 ^{13}C NMR (100 MHz, CDCl_3) spectrum of $\text{FeCp}_2\text{PPh}_2\text{RCN}$. Major isomer: δ 160.8, 154.2, 148.6, 138.8, 138.7, 137.4, 137.3, 135.6, 135.2, 135.0, 132.7, 132.5, 128.9, 128.0, 127.9, 127.6, 127.5, 127.1, 123.9, 121.3, 95.8, 75.9, 71.7, 69.6, 69.3, 69.1, 63.9, 63.8, 21.4.

CX5-H-X
P31CPD CDCl3 [D:\NMR400\02T2] run 7

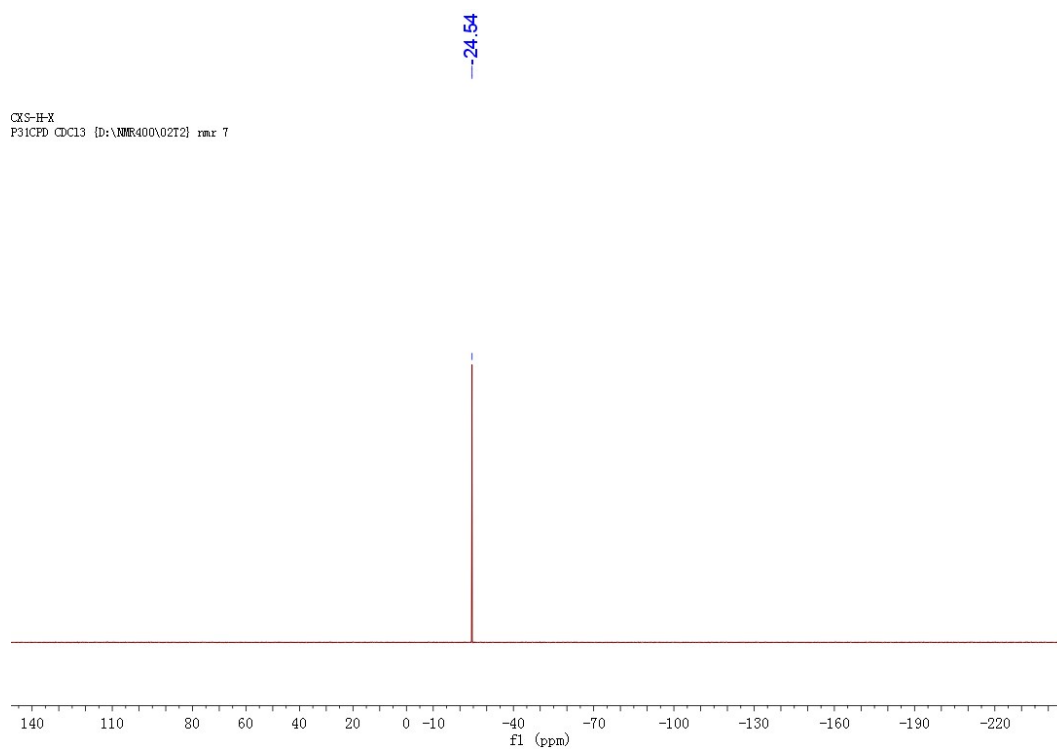


Fig. S3 ^{31}P NMR (162 MHz, CDCl_3) spectrum of $\text{FeCp}_2\text{PPh}_2\text{RCN}$. Major isomer: δ -24.

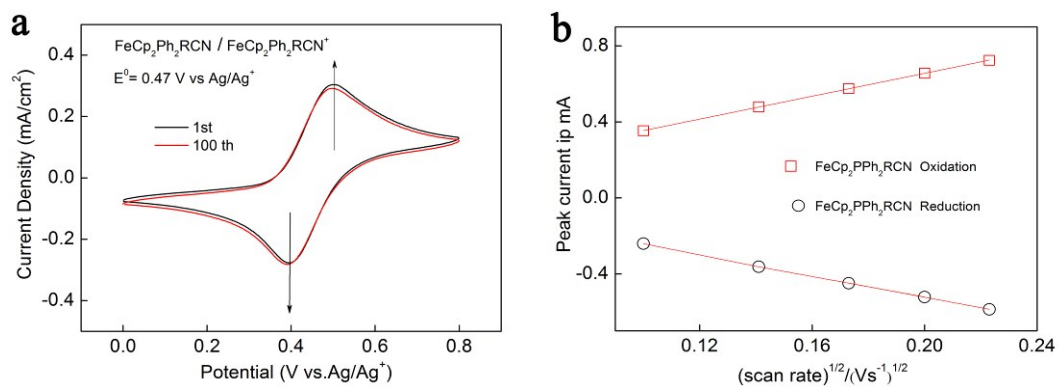


Fig. S4 (a) Cyclic voltammograms behavior of 0.005 M FeCp₂PPh₂RCN on glassy carbon electrode at 50 mV/s for 100 times. (b) Linear relationships between the oxidation and reduction peak current densities with the square root of the sweeping rate of FeCp₂PPh₂RCN.

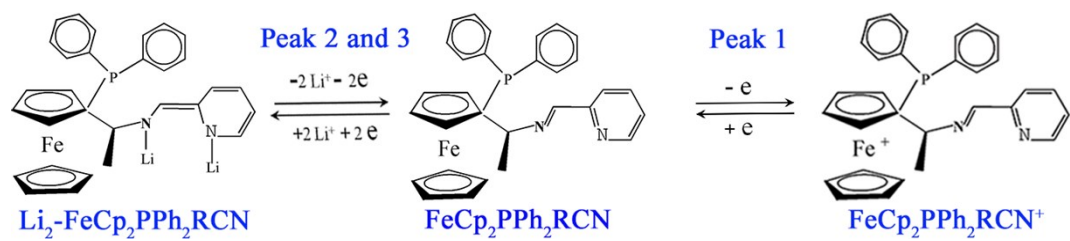


Figure S5. The electrochemical principle of $\text{FeCp}_2\text{PPh}_2\text{RCN}$.

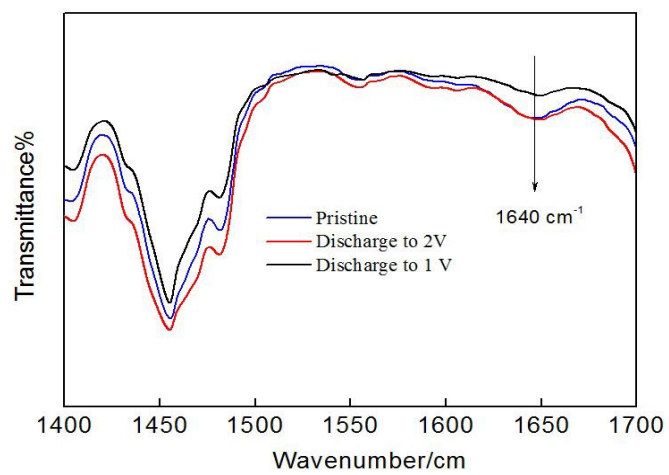


Fig. S6 (a) FTIR spectra of FeCp₂Ph₂RCN at different SOC.

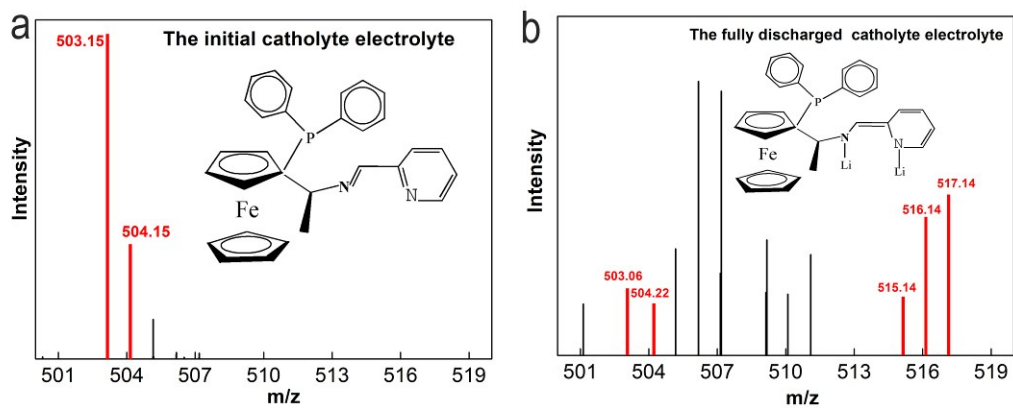


Fig. S7 ESI-MS of the original electrolyte (a) and the fully discharged positive electrolyte (b).

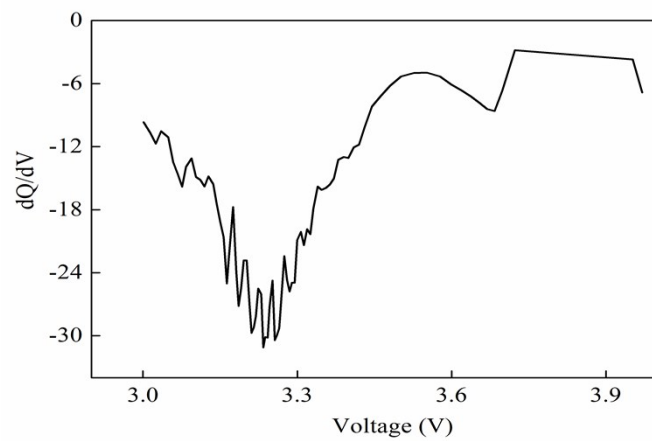


Fig. S8 Voltage derivatives of the capacity versus voltage during discharge process.

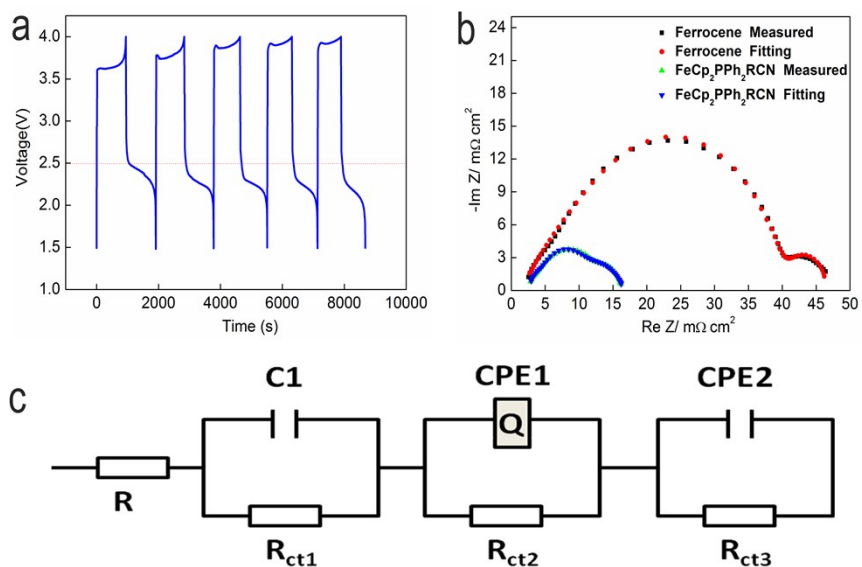


Fig. S9 (a) Charge and discharge plot of ferrocene at 10 mA/cm². (b) Impedance spectrum comparison of the cells assembled with ferrocene and FeCp₂PPh₂RCN. (c) Equivalent circuit of the cell that assembled with ferrocene and FeCp₂PPh₂RCN.

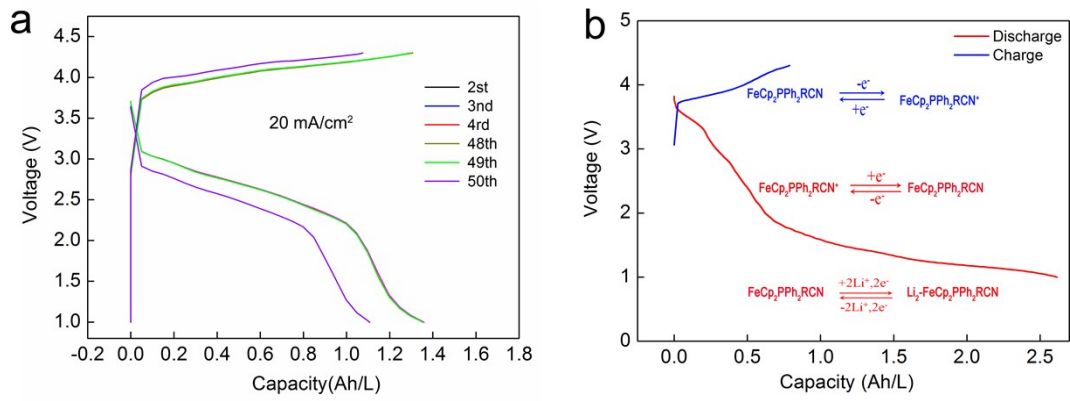


Fig. S10 (a) Voltage curves with the respect to the capacity at the current density of 20 mA/cm². (b) The charge and discharge capacity for the 1st cycle at the current density of 10 mA/cm².

Theoretical calculation and interpretation

In order to understand the intrinsic mechanism of ultra-high redox potential, obtained by ferrocene and its derivatives, a theoretical approach was carried out to determine the E^0 of $\text{FeCp}_2\text{PPh}_2\text{RCN}/\text{FeCp}_2\text{PPh}_2\text{RCN}^+$ couples in EC, DMC, EMC (vol 1:1:1) with 1M LiPF_6 . The E^0 of the oxidation–reduction system was obtained from the free energy change ΔG , which is linearly expressed as $\Delta G = -nFE^0$, where n is the number of electrons, F is the Faraday constant. Using $\Delta G = \Delta H - T\Delta S$, the entropy contributions to the total free energies of reaction have been neglected, and ΔH , the heat of formation at 0 K, is predicted by the density functional theory (DFT) calculation. Above all, E^0 can be described as $E^0 = -(nF)^{-1}\Delta H + b$, where b is a constant, and this method has been proved to be efficient at previous works. The difference of E^0 of ferrocene and its derivatives were estimated by positive reaction, using the following schematic equation, $\Delta E^0 = -(nF)^{-1}[(H_1 - H_2) - (H_3 - H_4)]$, and H_1 , H_2 , H_3 , H_4 represent the calculated heat of $\text{FeCp}_2\text{PPh}_2\text{RCN}^+$ ion, $\text{FeCp}_2\text{PPh}_2\text{RCN}$, Ferrocene ion, Ferrocene respectively.

The calculations were performed using DFT under the generalized gradients approximation (GGA), the Perdew Burke Ernzerhof (PBE) exchange correlation functional, and the projector augmented wave (PAW) method, as implemented in the Vienna Ab initio Simulation Package (VASP). During the procedure of geometry optimization, a cubic box of 25 Å along with gamma k-point sampling were used. The molecules were fully relaxed until the maximal residual force was $< 0.01 \text{ eV}/\text{Å}$, and the cut-off energy was set as 500 eV. Spin-polarization was included in all computations with 0.01 eV Fermi-level smearing.