Supporting Information for

Multicore Ferrocene Derivative as a Highly Soluble Cathode Material for Nonaqueous Redox Flow Batteries

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Experimental details

Materials

All dry solvents were stored in sealed flask with suitable molecular sieves after distillation. All chemicals were used as received without further purification. Ferrocene (Fc, 98%), phosphoric anhydride, phosphoric acid, methyl levulinate, Lithium aluminum hydride solution, Sodium hydride, 1-bromo-2-methoxyethane (98%), sodium sulfate (Na₂SO₄, 99%), sodium chloride (NaCl, 99.99%), bis(trifluoromethane) sulfonimide lithium salt (LiTFSI, 99.95%) and Tetrabutylammonium Tetrafluoroborate (TBABF₄, 98%) were purchased from Sigma-Aldrich. Methanol (MeOH, 99.9%) and Tetrahydrofuran (THF, 99.85%) were purchased from Acros. Deionized water after deoxidization was used for all experiments. ¹H NMR and ¹³C NMR spectra were recorded on a BrukerAvance 600 spectrometer, and the chemical shifts are reported as parts per million from TMS (*δ*). Mass spectra were acquired on HRMS (Bruker solanX 70 FT-MS).

Synthesis of 4,4-diphenylpentanoic acid methyl ester (DFE)

Polyphosphoric acid (PPA) was prepared by slowly adding phosphoric anhydride (12.5 g) to 85% phosphoric acid (12.5 g), followed by warming on the steam bath, with stirring, to obtain a solution. Methanol (14 ml) was added dropwise, with stirring, to the cooled acid and 15 ml of cyclohexane contained in a three-necked flask equipped with a constant-rate addition funnel, condenser, stirrer, thermometer, and nitrogen inlet, keeping the temperature below 60°C. Ferrocene (9.3 g, 0.05 mol) was introduced into the flask all at once and the stirred mixture heated in an oil bath maintained at 98-100°C throughout the reaction. Methyl levulinate (9.75 g, 0.075 mol) was added dropwise with vigorous stirring during 24 h; ca. 0.02 mol was added during the first 2 h and the remainder at a constant rate until all added; temperature 76-78°C within the mixture throughout the reaction. After cooling to 25°C, the mixture was stirred with 50 ml each of water and benzene. The deep-orange upper layer was separated from the dark-green lower layer which was extracted twice with benzene. The combined organic solutions were washed successively with brine and the organic phase was dried over Na₂SO₄. After filtration and removal of the solvents under reduced pressure, the residue was purified by flash chromatography (N-hexane/Ethyl acetate, 11:1) to afford compound MFP (8.46 g, 71%) as a red-brown oil. ¹H NMR (600 MHz, cdcl₃) δ 4.11 (s, 16H, Cp-Cp'e), 4.00 (s, 2H, Cp'e), 3.64 (s, 3H,

CH₃O), 2.28 (s, 2H, CH₂), 2.18 (s, 2H, CH₂), 1.56 (s, 3H, CH₃C); ¹³C NMR (600 MHz, CDCl₃) : δ 174.66 (C=O), 99.73 (Fc-C-Fc), 68.62 (Cp), 66.91, 66.34 (Cp'e), 66.74 (Cp'e-C), 51.55 (CH₃O), 38.32 (CH₂), 30.13 (CH₂), 24.26 (CH₃); HRMS (m/z): Calcd for C₂₆H₂₈Fe₂O₂: 484.078322. Found: 484.078278.

Synthesis of 4,4-diferrocenylpentan-1-ol (DFO)

Powdered LiAlH₄ (0.95 g, 25 mmol) was added to the ice-cooled solvent under nitrogen atmosphere. A solution of distilled **DFE** (8.1 g, 16.7 mmol) in dry THF (100 mL) was placed in a dropping funnel and was added to the stirred ice-cooled suspension of the reductant dropwise. After the addition was completed, the reaction mixture was allowed to come to ambient temperature (0.5 h) and was heated with a water-bath to 40 °C for 8 h. The progress of the reaction can be monitored by TLC. After the reaction was complete, it was dripped into ice-cooled water (200 mL) by inches in order to quench this reaction. Then, the aqueous phase was extracted with EA (3×200 mL) and the organic phase was dried over Na₂SO₄. The solvent was evaporated in vacuo to yield dark-red solid (6.94 g, 91%). Without further purification, its purity can meet the need of next reaction.

Synthesis of 4,4-diferrocenyl-1-(2-Methoxy-ethoxy)-pentane (DFDE)

To a solution of **DFO** (6.85 g, 15 mmol) in dry THF (120 mL) was added Sodium hydride (0.9 g, 22.5 mmol) under nitrogen atmosphere. The reaction mixture was then stirred for 1 h at room temperature. Next, 1-bromo-2-methoxyethane would be added by dripping slowly at room temperature when the solution had become dark-green. The mixture was stirred at room temperature overnight. After the reaction monitored by TLC was completed, it was poured into ice-cooled water (100 mL) for redundant Sodium hydride consumed and extracted with EA (3 × 100 mL). The combined organic layers were washed with brine (20 mL), dried over Na₂SO₄, and concentrated under the reduced pressure to give a dark-brown oil. Later, the dark-red syrup was purified by column chromatography (N-hexane/Ethyl acetate, 10:1) to afford compound **d** (1.75 g, 82%) as a red oil. ¹H NMR (400 MHz, CDCl₃): δ 4.03 (s, 16H, Cp), 3.93 (s, 2H, Cp'e-C), 3.46 (s, 4H), 3.33 (d, *J* = 6.8 Hz, 2H, CH₂), 3.31 (s, 3H, CH₃O), 1.83 – 1.75 (m, 2H, CH₂), 1.51 (s, 3H, CH₃C), 1.49 (s, 2H, CH₂). ¹³C NMR (400 MHz, CDCl₃): 100.88 (Fc-C-Fc), 72.10 (Cp), 69.92, 68.85 (Cp'e), 66.84 (Cp'e-C), 59.13 (CH₃O), 39.99 (CH₂), 36.02 (CH₂-O-CH₂), 24,96 (CH₂), 24.47 (CH₃); HRMS (m/z): Caled for C₂₈H₃₄Fe₂O₂: 514.125281. Found: 514.125223.

Cyclic voltammetry (CV) studies

Electrochemical measurements were conducted on the three-electrode system of electrochemical station (Gamry reference 3000), which was constituted by A glass carbon working electrode (Shanghai Chu Xi Industrial Co., Ltd.) with the diameter of 3 mm, A platinum wire was served as the counter electrode (Jiangsu Shenzhou carbon product Co., Ltd) and a Ag/AgCl reference electrodes (Shanghai Huachen Instrument Co., Ltd.). The cyclic voltammetry (CV) was tested on 5 mM DMDF and 10 mM BFD in 0.5 M TBABF4 ACN with scanning rates from 50 mV s⁻¹.

RDE studies

RDE measurements were operated via a rotating disk electrode (RRDE-3A, ALS Co. Ltd.), which included in a Ag/AgCl electrode as the reference electrode, a platinum wire as the counter electrode and a three-electrode configuration with a glassy-carbon disk (3 mm in diameter) as the working electrode. RDE profiles were acquired under the different rotating speeds with a fixed sweeping rate of 10 mV s⁻¹. The rotation speeds for the catholyte were 900, 1225, 1600, 2025, 2500, 3025 and 3600 rpm. η used for the calculation of k_0 was 40, 50, 60, 70 and 80 mV.

Using the slopes of the linearly fitted Levich plots (Figure 5d) and the Levich equation (Equation 2), the diffusion coefficients (*D*) of DFDE and DFDE⁺ were calculated. Using the Koutecký-Levich equation (Equation 2), Koutecký-Levich plots (Figures 5b and c) were obtained.

$$i_L = 0.62nFAD^{2/3}\omega^{1/2}v^{-1/6}C_0$$
 [1]

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C_0}$$
[2]

$$i_0 = 0.62nFAk_0C_0$$
 [3]

Here, *n* is the number of electrons transferred (*n*=1), *F* is the Faraday constant (F = 96485 As mol⁻¹), *A* is the electrode area (A=0.0707 cm²), and C_0 is the concentration of the DFDE ($C_0 = 0.5$ mM).

Determination of the solubility of (DFDE)

To determine the solubility of DFDE in bare DME and ACN solvent, excess DFDE (0.2 g) was separately added to the 2 ml DME and 2 ml ACN, respectively. After stirring for sufficient time, the upper clear solution was transferred into a volumetric flask (1 mL) and vaporized in vacuum at room temperature. The remaining DFDE was weighed to be 1.18 g and 0.272 g, respectively, corresponding to a molar concentration of 2.3 M in DME and 0.53 M in ACN, respectively.

UV-vis spectroscopy

For the UV-vis spectroscopy analysis, absorption spectra of the electrolytes in the positive electrode compartment (diluted in MeCN, 5% v/v) were obtained using a UV-vis spectrometer (Agilent Technologies, Cary 5000) with an optical glass cuvette (Quartz; Hellma). Electrolytes containing 50 mM DFDE and 100 mM BuPh in the supporting electrolyte of 0.5 M TBABF₄ in MeCN were used.

Static half-cell test

A half-cell was assembled with two quartz shells (1 mm thick, 8 mm in diameter) and a NASICON-type $Li_{1+x+3z}Al_x(Ti, Ge)_{2-x}Si_{3z}P_{3-z}O_{12} Li^+$ - ion conducting membrane (LICGC® AG-01, Ohara Corp., Japan) sandwiched in between. The components were sealed together with Surlyn® resin (Solaronix Meltonix 1170-25). A Ti foil precasted with a Super P carbon/PVDF thin layer was used as the current collector for the cathode, and a piece of Li foil pressed onto the Cu foil was used as the anode. The electrolyte was injected into the quartz shell chamber through a small hole on the Ti or Cu foil. The electrolyte used at the anode was 1 M LiTFSI in DME, whereas the electrolyte used in the cathode was 0.1 M DFDE in DME containing 1 M LiTFSI and 1 M DFDE in DME containing 2.5 M LiTFSI, respectively.

Static full cell test

The cell was assembled with a piece of Daramic 175[®] sandwiched between two quartz shells (1 mm thick, 8 mm in diameter), graphite felts (7 mm diameter and 1.5 mm thickness) and Ti foil pre-casted with a Super P carbon/PVDF thin layer. All cell tests were carried out at room temperature on a potentiostat (BT-2043, Arbin instruments).

Calculation method

The structure optimization was performed with Gaussian 09 software package [1], Data analysis and picture drawing were using Multiwfn [2] and VESTA, The structure optimization using the b3lyp as the functional, hybrid basis set was set with lanl2dz for Fe atom and 6-31g (d,p) for C, H, O atoms, respectively [1, 3-5]. Implicit solvent model of SMD were performed to account the solvation effect of acetonitrile using m062X functional. Electronic spin density was calculated using the non-restrictive open-shell method to eliminate the possibility of spin-polarized singlet state in the +1 and +2 valence

states with guess = mix to break the symmetry of frontier molecular orbitals.



Figure S1. ¹H NMR spectra of DFE.



Figure S2. ¹³C NMR spectra of DFE.



Figure S3. ESI-MS of DFE.



Figure S4. ¹H NMR spectra of DFDE.

Figure S5. ¹³C NMR spectra of DFDE.

Figure. S6. ESI-MS of DFDE.

Figure S7. Calculated solvation free energy of Ferrocene, Di-core ferrocene and DFDE, respectively.

Molecule	Number of	Electrolute	Solubility	Redox potential V	Ref.
	electrons	Electrolyte	(M)	(vs. Fc/Fc ⁺)	
Fe Fe	1	1.2 M LiTFSI/EC/PC/EMC (4:1:5)	0.04	0	[6]
Fe N+	1	1.2 M LiTFSI/EC/PC/EMC (4:1:5)	0.85	0.2	[6]
$ \begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & $	1	EC/PC/EMC (4:1:5)	0.4	~ 0.2	[7]
$ \underbrace{Fe}_{Fe} \xrightarrow{N_{+}} Clo_{4}^{-} $	1	EC/PC/EMC (4:1:5)	0.63	0.15	[7]
	1	EC/PC/EMC (4:1:5)	2.08	NA	[7]
Fe PF ₆	1	EC/PC/EMC (4:1:5)	1.71	0.14	[7]
Fe CH ₃	1	EC/DEC at 50°C	3	-0.05	[8]
Fe	1	1.0 M TEAPF ₆ /CAN	< 0.5	0.18	[9]

Table. S1. Summary of ferrocene-based redox species for NARFBs applications

Fe CH ₃	1	1.0 M LiPF ₆ /PC	0.81	0.21	[10]
Fe N N	2	1.0 M LiPF6/EC/PC/EMC (1:1:1)	~ 0.6	0.58	[11]
Fe CI	1	H ₂ O	4	0.61 V vs. SHE	[12]
Fe Nt 2Br	1	H_2O	3.1	0.61 V vs. SHE	[13]
Fe N+	1	H_2O	1.9	0.39 V vs. SHE	[13]
	4	ACN/THF (4:1)	> 0.25	0.15 V vs. Ag/AgNO3	[14]
Pre-	2	DME	2.3	0.08	This
		CAN	0.53	0.12	work

Figure. S8. Photo of the static half-cell device

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Figure. S9. Charge-discharge behaviors of DFDE | Li half-cell. Coulombic efficiency and charge–discharge capacities versus time and cycle number using the catholyte containing 0.1 M DFDE (a) and 1 M DFDE (c). Charge–discharge under galvanostatic conditions using the catholyte containing 0.1 M DFDE (b) and 1 M DFDE (d).

Figure. S10. Photo of the static full cell device.

Figure S11. CV curves of DFDE and BuPh electrolyte at 50 mV s⁻¹.

Figure S12. Charge-discharge behaviors of DFDE | BuPh cell. (a) Representative first ten charge/discharge voltage profiles over time of the symmetric static cell. (b) Coulombic efficiency and charge–discharge capacities versus time and cycle number. The electrolyte used in the symmetric cell is an acetonitrile solution containing 0.45 M DFDE, 0.9 M BuPh and 1.2 M TBABF4. The current density is 20 mA cm⁻².

Figure S13. UV-vis spectra corresponding to the colors of the BFD at the given SOCs.

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