

## **Electrochemical Oxidation of Double-Stranded Bis-Polynorbornenes Containing Linearly Aligned Ferrocene Linkers**

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### **Experimental**

**Cyclic voltammetry and differential pulse voltammetry.** A conventional three-electrode system with a potentiostat/galvanostat (Eco Chemie, microAutolabIII) was employed for cyclic voltammetric and differential pulse voltammetric experiments. A Pt disk electrode (diameter 2 mm), a Pt wire, and an Ag/Ag<sup>+</sup> (10 mM AgNO<sub>3</sub>) were used as the working, the counter and the reference electrodes, respectively. Sample was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M nBu<sub>4</sub>NPF<sub>6</sub>, and the electrolyte was purged with Ar for at least 10 min before electrochemical experiments. All the potentials reported in the text were referred to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple, which potential was measured after every electrochemical experiments.

**Chronoamperometric bulk electrolysis.** A tube-shaped Pt web working electrode (52 mesh, diameter 5 mm, height 5 mm) surround by a coaxial tub-shaped Pt foil counter electrode (diameter 8 mm, height 5 mm) with an Ag/Ag<sup>+</sup> (10 mM AgNO<sub>3</sub>) reference electrode placed at 1 mm above the center of the working electrode was employed for bulk-electrolysis experiments. A CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> and specified amount of sample was stirred by a magnetic stir bar at 5 mm below the working electrode throughout the entire electrolysis process. A constant potential was applied to carry out the electrochemical oxidation, and the electrolysis process was stopped when a steady-state current response around zero was reached. The charge consumption was calculated by integrating the area under the *i-t* curve.

The experiment details are summarized in Table 3.

Table 3. The experiment details of bulk-electrolysis of the ferrocene containing polymers.

	$M_n$	Amount taken (mg)	Monomer molecular weight	Ferrocene units <sup>c</sup> ( $\mu\text{mole}$ )	Applying potential (V)	Total charge consumed (C / $\mu\text{mole}$ )
<b>3a</b>	13700	13.1	721	18.2	0.35	1.31 / 13.6
<b>3b</b>	31100	4.7	777	6.0	0.35	0.39 / 4.1
<b>3c</b>	31200	5.0	873	5.7	0.35	0.38 / 3.9
<b>4</b>	1700	10.2	212	48.1	0.35	4.88 / 50.5
<b>4</b>	11900	7.2	597	12.1	0.40	0.80 / 8.3

<sup>c</sup> The amount of ferrocene units employed in the bulk-electrolysis was estimated by dividing the molecular weight of polymer used over the molecular weight of its corresponding monomer.

**Chronoamperometric experiment at microelectrode.** A microdisk working electrode (diameter 10  $\mu\text{m}$ ), a Pt wire counter electrode and an Ag/Ag<sup>+</sup> (10 mM AgNO<sub>3</sub>) reference electrode with a potentiostat/galvanostat (EG&E, PAR 273A) were employed for potential-step experiments. The sample was dissolved in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>, and purged with Ar for at least 10 min before each experiment. The applying potential was firstly maintained at the open-circuit voltage (-0.15 V) for 5 sec then step to a desired potential (0.25 V for **3b** and **3c**, 0.35 V for **4**) for 35 sec, and the *i-t* response was recorded. The diffusion coefficients were estimated to be 1.19 x 10<sup>-6</sup>, 1.04 x 10<sup>-6</sup>, and 2.05 x 10<sup>-6</sup> cm<sup>2</sup>/sec for **3b**, **3c**, and **4**, respectively. The electrochemically oxidized **3a** and **4** were seriously deposited onto the microelectrode surface, therefore the electron transfer numbers and diffusion coefficients could not be estimated.

**Polymer radical cation.** Compound **3a** was electrolyzed according to the method mentioned above. The oxidized **3a**, insoluble in CH<sub>2</sub>Cl<sub>2</sub>, was filtered and washed three times by CH<sub>2</sub>Cl<sub>2</sub>, and then dried under vacuum.

**Magnetic Measurements.** The magnetization data were recorded on a SQUID magnetometer (MPMS7 Quantum Design company) with an external magnetic field of 1.0 Tesla in the temperature range of 2K to 295K. The diamagnetic background of sample holder was measured at the same experimental condition before the sample was measured. The magnetic susceptibility data were corrected for diamagnetism by the tabulated Pascal's constants.

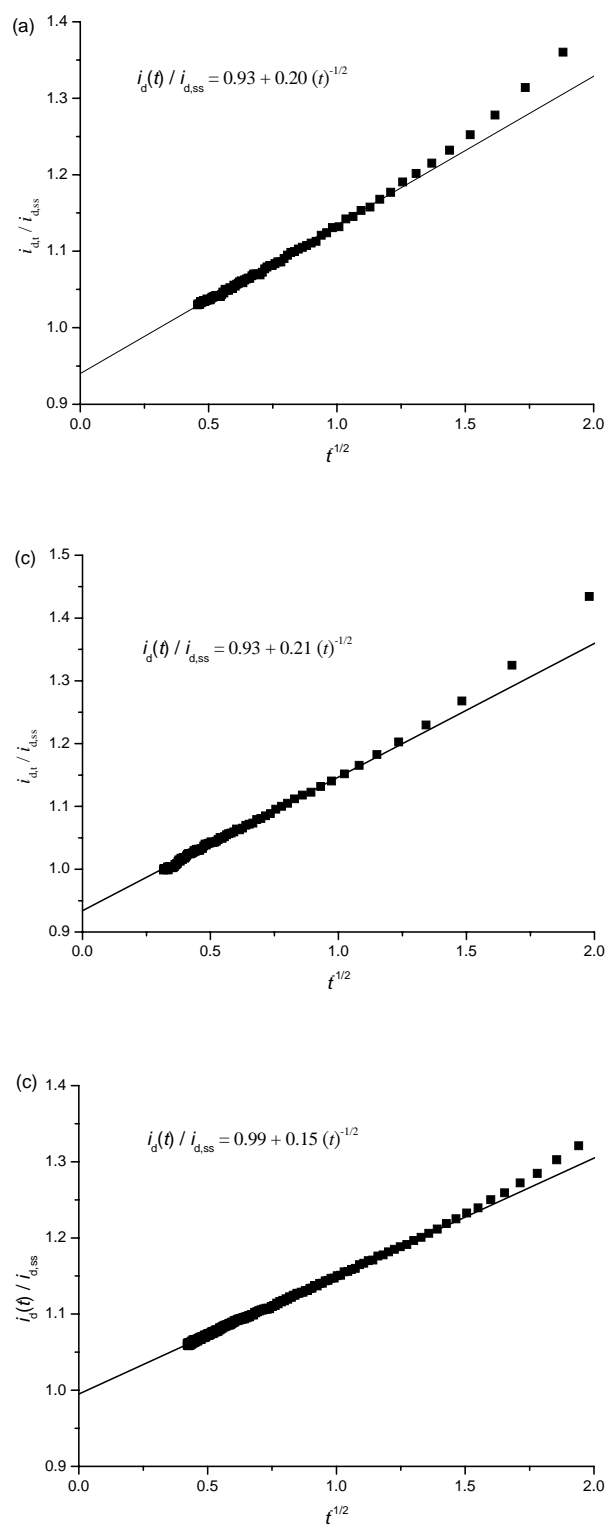
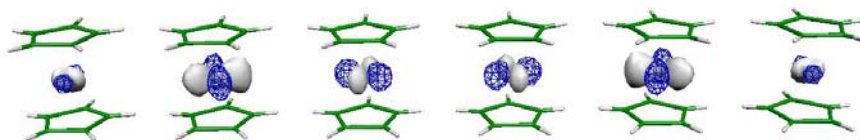
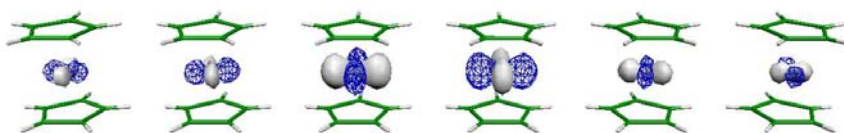


Figure S1.  $(i_d(t) / i_{d,ss})$  vs.  $(t^{-1/2})$  plots of (a) **3b**, (b) **3c**, and (c) **4** in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M  $\text{Bu}_4\text{NPF}_6$ .  $i_d(t)$ : chronoamperometric current response at a microdisk electrode.  $i_{d,ss}$ : steady-state current response at a microdisk electrode.

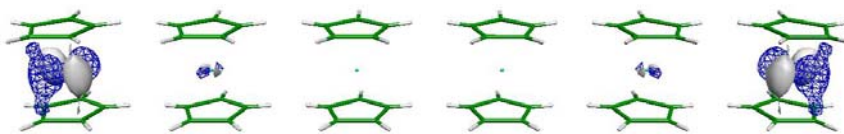
$E(\text{HOMO-5}) = -4.3283 \text{ eV}$



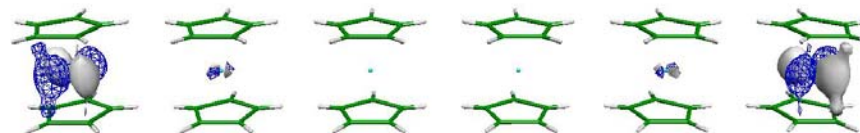
$E(\text{HOMO-4}) = -4.3107 \text{ eV}$



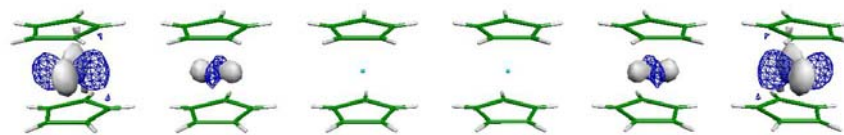
$E(\text{HOMO-3}) = -4.2877 \text{ eV}$



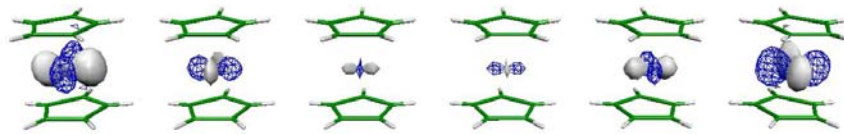
$E(\text{HOMO-2}) = -4.2877 \text{ eV}$



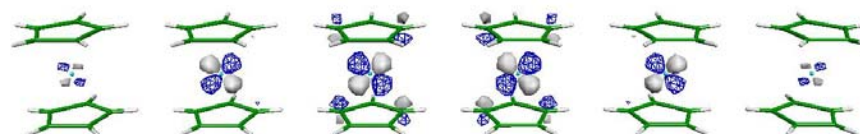
$E(\text{HOMO-1}) = -4.2782 \text{ eV}$



$E(\text{HOMO}) = -4.2773 \text{ eV}$



$E(\text{LUMO}) = -1.6021 \text{ eV}$



$E(\text{LUMO+1}) = -1.5551 \text{ eV}$

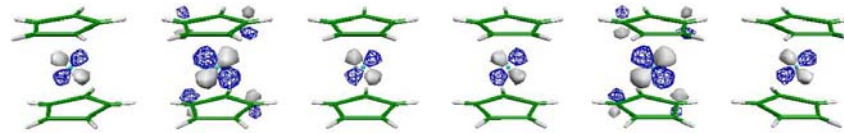


Figure S2. Selected frontier orbitals of **5**.