Hole-Transporting Property of Star-shaped Nitroxide Radical Molecule

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Keywords: Radical Molecule, Hole-Transporting Material, Star-shaped Molecule.

1. Introduction

Hole-transporting organic molecules have been extensively studied for their application to organic electric devices including organic light-emitting diodes [1], field effect transistors [2], and photovoltaic cells [3]. Requisites of the hole-transporting molecule applicable to organic electric devices are chemical and electrochemical stability, high hole-mobility, and feasible ionization potential for the hole-injection from an electrode metal. Arylamines and polythiophene derivatives have been served as the hole-transporting material. From a chemical viewpoint, the hole-transport could be ascribed to an anodic redox on the highest occupied molecular orbital (HOMO) of the molecule, yielding the corresponding cationic radical. However, to the best of our knowledge, there has been no report on a hole-transporting process based on a singly occupied molecular orbital (SOMO) of neutral radical molecule, except our previous report [4].

In this paper, we describe hole-transporting property of a star-shaped triradical molecule, 1,3,5-tris(4-methoxyphenyl-4'-*tert*-butyl-oxyamino phenyl)aminobenzene **1**, as a model compound of a hyper-branched polyradical molecule **2**. The polyradical **2** and **1** are expected to display hole-transporting property based on both the amine and radical moieties. Additionally, the hyper-branched or star-shaped structure probably realizes high glass-transition temperature affording amorphous stability of their solid film.

2. Experimental

Materials

N-(*tert*-Butyl-*N*-triisopropylsilyloxy)amino-benzene **3** [5] and 1,3,5-tris(*N*-(4-methoxyphenyl)-aminobenzene **4** were prepared according to the literature [6]. The novel triradical molecule **1** was synthesized by palladium-catalyzed coupling of **3** and **4** followed by deprotection and chemical oxidation.

1 : MS: m/e 929.6 (M^+ , found). Found: C, 74.0; H, 6.8; N, 8.8 %. Calcd for $C_{57}H_{63}N_6O_6$: C, 73.8; H, 6.8, N, 8.9 %.

Fig. 1 Schematic diagram of hopping conduction on SOMOs.

Fig. 3 ESR spectrum of the triradical **1** in 20mM THF solution.

Electron spin resonance (ESR), UV-vis spectra, and cyclic voltammetry (CV) were recorded by using JEOL JES-TE200 ESR spectrometer, JASCO V-550 UV/vis spectrophotometer, and BAS 100B/W electrochemical analyzer, respectively.

Device fabrication

16 mM THF solution of triadical **1** with 0.1% polycarbonate (PC) (10g/l) was spincoated on an ITO (indium tin oxide) glass substrate, followed by vapor deposition of gold on the organic layer. Current-voltage characteristic was measured by using a 2400-C digital source meter (Keithley).

3. Results and Discussion

A multiplet ESR signal was observed at $g = 2.0060$ for THF solution of the triradical **1**. Cyclic voltammetry and differential pulse voltammetry of **1** exhibited reversible redox waves at 0.17, 0.28 and 0.46 (V vs. ferrocene/ferrocium⁺). During the electrochemical oxidation, the ESR signal intensity decreased on the anodic side, suggesting the electron on SOMO is oxidized at the first oxidation potential. UV-vis absorption peaks (amine $n-\pi^*$, $\lambda_{\max} = 300$ nm, nitroxide $\pi-\pi^*$, $\lambda_{\max} = 355$ nm) decreased gradually under the applied potential, and new absorptions appeared at 416 and 585 nm which were attributed to a quinonoid structure of the cationic state. Ionization potential of **1** was estimated to be 5.1 eV by the photoelectron spectroscopy. These results suggest possibility of an effective hole-injection into the organic radical from anode metals (ITO, Au). Current-voltage (I - V) characteristic of a hole-only device (Fig. 4) gave

maximum current density of 48 mA/cm² at 30 V, which means an effective hole-injection and transporting properties the triradical molecule **1**.

Fig. 4 Current density-electric field characteristic of a hole-only device configured with ITO/1:PC (150 nm)/Au(150 nm).

Acknowledgement

This work was partially supported by Grant-Aid for Scientific Research (No.17067017) from MEXT, Japan.

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