An unpaired electron-based hole-transporting molecule: Triarylamine-combined nitroxide radicals†

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A durable nitroxide radical combined with a triarylamine moiety exhibited a hole-drift mobility of 6×10^{-3} cm^2 V^{-1} s^{-1}, to which the aminophenyl nitroxide structure contributed.

Hole-transporting organic molecules have played an important role in organic electronic devices, such as organic light-emitting diodes,[1] field-effect transistors[2] and photovoltaic cells.[3] The requisites of such hole-transporting molecules include a reversible redox property with a low ionization potential and a high hole drift mobility in an amorphous state.[4] Aromatic compounds, such as arylamine[5] and thiophene[6] derivatives, have been explored as hole-transporting molecules, and hole drift mobilities as high as 10^{-3}–10^{-2} cm^2 V^{-1} s^{-1} have been reported for triphenylamine-combined thiophene derivatives,[7] a value which has been considered the highest limiting value of hole drift mobility in the amorphous state.[4] These compounds possess a closed shell electron configuration and form the corresponding cationic open shell radicals (or "holes") *via* their one-electron oxidation, or by hole-injection from an anode by an applied voltage. Hole-transporting in these molecules is categorized as hopping conduction, which could be described from the viewpoint of a chemical reaction formula as an intermolecular repetitive redox reaction between the neutral closed shell starting molecule and its cationic open shell radical. However, to the best of our knowledge, hole hopping using an unpaired electron on the singly-occupied molecular orbital (SOMO) of an organic radical molecule with an open shell electron configuration[8,9] has not been reported. That is, we expected hole hopping based on a repetitive redox or electron exchange between the neutral radical molecule of the SOMO configuration and the formed cationic molecule of the unoccupied closed shell configuration. Such radical- or unpaired electron-based hole hopping could be attractive because of the possible realization of a new effective hole-transporting molecule, with a lower oxidation potential compared to those of previously known hole-transporting closed shell aromatic compounds.

Very recently, we reported durable nitroxide radical molecules as a new class of cathode-active materials for a secondary battery, where the very rapid redox reaction of the unpaired electron on the nitroxide radical was successfully utilized for the charging–discharging process of a high rate battery.[10] However, this application of nitroxide radicals was realized in the presence of an electrolyte solution under wet conditions. Hole hopping based on the redox reactions of radical molecules in dry or solvent-free amorphous states have not been examined to date. Furthermore, the ionization potential of typical nitroxide radical molecules has been estimated to be around -5.2 eV,[11] which is slightly higher than those of previously reported hole transporting molecules, and is expected to be appropriate for hole injection from an anode, compared to other typical hole-transporting molecules.

In this paper, we describe for the first time the hole-transporting properties of nitroxide radical molecules in an amorphous solid state by synthesizing new radical molecules, *i.e.*, *N*,*N*-bis(4-methoxyphenyl)-4-(*N*-*tert*-butyl-*N*-oxyamino)phenylamine (**1**), *N*,*N*-bis(4-methoxyphenyl)-4-(1-oxyl-3-oxide-4,4,5,5-tetramethyl-imidazolin-2-yl)phenylamine (**2**) and *N*-{4-(*N′*-*tert*-butyl-*N′*-oxyamino)phenyl}-*N*-(4-methoxyphenyl)-4-(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)phenylamine (**3**) (Fig. 1). Nitroxide radical molecules **1** and **3** were expected to possess the following characteristics: (i) A high hole mobility, additionally induced by an intermolecular overlapping among the delocalized π-electrons over the entire molecule, (ii) a possible redox property at a low oxidation potential due to the aminophenyl nitroxide structure and (iii) a high thermal and chemical durability during device fabrication. The nitronyl nitroxide **2**[12] was prepared as the control compound.

The radical molecules were prepared *via* several steps from 4-bromophenyl-*N*-*tert*-butyl-*N*-siloxyamine,[13] *N*,*N*-bis(4-methoxyphenyl)aniline and 4-bromobenzaldehyde.† These radicals were durable under ambient conditions (half life time $t_{1/2} > 6$ months).[14]

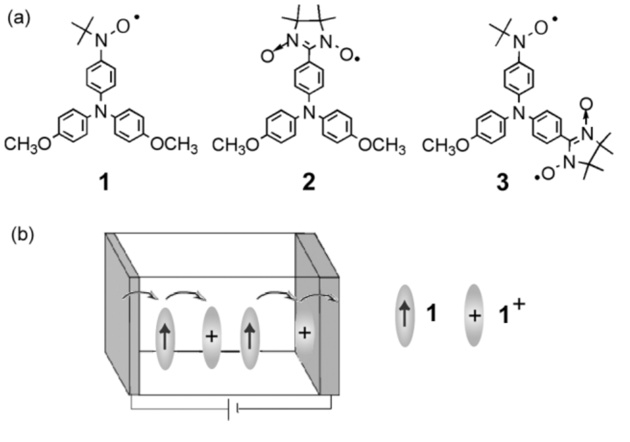

Fig. 1 (a) Chemical structures of the radical molecules and (b) schematic hole-transporting mechanism of **1**.

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The cyclic voltammograms of **1** and **3**, with their typical electrolytic ESR signals, are shown in Fig. 2. The monoradical **1** showed a reversible unimodal redox couple at −0.25 V (*vs.* Fc/Fc$^+$), and a three-lined ESR signal was observed at g = 2.006, with the hyperfine coupling constant (a_N) of 1.30 mT under −0.4 V, which disappeared with the application of an anodic potential over 0.1 V. This redox couple of **1** was assigned to the oxidation of the unpaired electron on the SOMO and the reduction of the closed shell cation **1**$^+$ formed. On the other hand, the diradical **3** displayed a multiplet signal at g = 2.0057 at a potential of −0.50 V (Fig. 2(b)). The simulation, with a strong exchange limit $|J| > |a|$ (J = intramolecular exchange interaction) between the unpaired electrons, gave hyperfine coupling constants of a_{NO} = 0.65 mT for the nitrogen of the nitroxide moiety and a_{NN} = 0.38 mT for the two equivalent nitrogens of the nitronyl nitroxide moiety. The initial multiplet ESR signal changed to a simple quintet signal with an intensity ratio = 1 : 2 : 3 : 2 : 1 and a_{NN} = 0.76 mT (twice that of the a_{NN} for **3**) in the potential region −0.10–0.20 V. These results indicated formation of the cationic radical **3**$^+$ and the localization of the unpaired electron on the nitronyl nitroxide moiety.[15] While applying a potential of 0.20–1.00 V, the ESR signal intensity decreased, ascribed to the formation of the corresponding closed shell dication **3**$^{2+}$. The energy gap between the two SOMOs of the nitroxide moiety and the nitronyl nitroxide moiety in molecule **3** was estimated to be 0.55 eV, based on the formal redox potentials ($E_{1/2}$ = −0.14 and 0.41 V). Cyclic voltammetry of monoradical **2** revealed two oxidation potentials at 0.23 and 0.49 V. The former was assigned to the redox of the triphenylamine, based on the electrolytic UV-vis absorption spectroscopy,[12] and the latter oxidation was due to the nitronyl nitroxide; the first one-electron oxidation of **2** was ascribed to the oxidation of the unpaired electron on the nitronyl nitroxide moiety.

The ionization potentials (I_p) of **1**, **2** and **3** obtained from photoelectron spectroscopic measurements were −4.9, −5.4 and −5.1 eV, respectively. The I_p values of **1** and **3** were comparable to that of copper phthalocyanine (I_p = −5.1 eV[16]), which could have originated from the aminophenyl nitroxide structure of **1** and **3**, suggesting a low hole injection barrier at the indium tin oxide (ITO) anode (−4.9 eV)/radical layer interface.

The hole-drift mobility of radicals **1**, **2** and **3** in polycarbonate was measured by the time-of-flight method, as shown in Fig. 3. Fig. 3 also shows the control hole-drift mobility data for the equivalent mixture of tris(4-methoxyphenyl)amine and *N-tert*-butyl-*N*-(4-*tert*-butylphenyl)oxyamine, which are the components of the triarylamine-combined nitroxide radical molecule **1**. The hole-drift mobilities of **1** and **3** were 5.8 × 10^{-3} and 7.8 × 10^{-3} cm^2 V^{-1} s^{-1} (at 0.47 MV cm^{-1}), respectively, which are 10^4 times higher than that of the control mixture (10^{-7} cm^2 V^{-1} s^{-1}) and comparable to the previously reported mobility (1.1 × 10^{-3} cm^2 V^{-1} s^{-1}) of a typical hole-transporting molecule, *e.g.*, *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-(1,1′-diphenyl)-4,4′-diamine.[17] This result indicates that the combined-molecular structure of triarylamine and nitroxide radical or the aminophenyl nitroxide structure in **1** and **3** has an excellent hole-transporting property. The extended π-conjugation, involving an unpaired electron over the aminophenyl nitroxide structure, could contribute to intermolecular overlapping to yield the high hole-drift mobility. On the other hand, the nitronyl nitroxide-combined triarylamine **2** has a localized unpaired electron, resulting in a one-order lower mobility than those of the nitroxide-combined triarylamines **1** and **3**. Current density (J) *vs.* electric field (E) plots for **1** and **3** in the hole only devices ITO/radical:polycarbonate/Au showed a gradual increase with the applied voltage, which supports both the hole-injection and hole-transporting capabilities

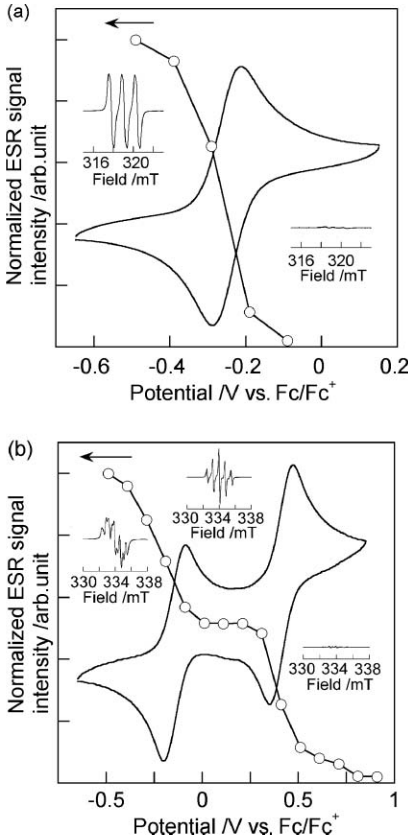

Fig. 2 Normalized ESR intensity with cyclic voltammograms of (a) **1** and (b) **3** in dichloromethane solution (supporting electrolyte $(C_4H_9)_4NBF_4$, Pt wire, Ag wire working electrode, quasi-reference electrode referenced to Fc/Fc$^+$). Inset: ESR signals during the electrochemical oxidation.

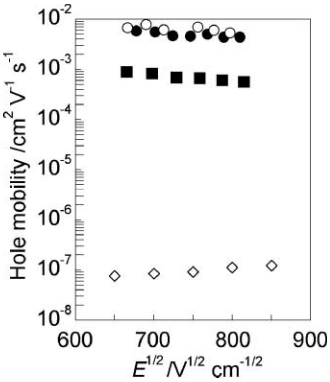

Fig. 3 Hole-drift mobility *vs.* electric field plots of the monoradical **1** (●), **2** (■), diradical **3** (○), and the blended film containing *N-tert*-butyl-*N*-(4-*tert*-butylphenyl) nitroxide and tris(4-methoxyphenylamine) (◇). Device configuration: ITO/radical:polycarbonate (4–6 μm)/copper phthalocyanine (100 nm)/Al (20 nm).

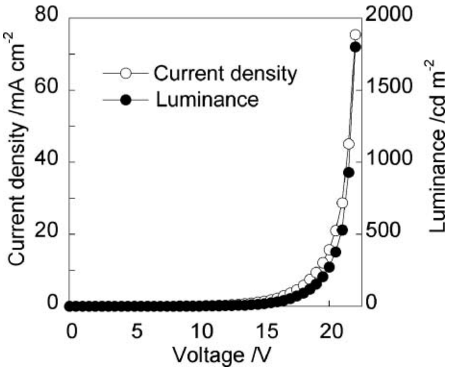

Fig. 4 Current density–luminance–voltage characteristics of the OLED device with configuration ITO/**1**:polycarbonate (20 nm)/NPD (40 nm)/Alq$_3$ (60 nm)/Ca (20 nm)/Al (100 nm).

of the nitroxide radical molecules. We have fabricated an OLED device using **1** as the hole-injection layer, ITO/**1**:polycarbonate/*N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPD)/tris(8-hydroxyquinoline) aluminum (Alq$_3$)/Ca/Al. The device including **1** exhibited a yellowish-green emission, with a maximum intensity of 1800 cd m^{-2} at 22 V (Fig. 4), which exceeded that of a control device, ITO/CuPc:polycarbonate/NPD/Alq$_3$/Ca/Al (250 cd m^{-2} at 22 V). This result indicates that the triarylamine-combined nitroxide radical molecule is a promising candidate for an efficient hole-transporting material.

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