The First Organic Radical Compounds Exhibiting n-Type FET Properties

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A couple of naphthalenediimide derivatives carrying TEMPO radicals were found to exhibit n-type FET with mobilities up to $2.6 \times 10^{-5}\,\mathrm{cm^2/V{\cdot}s}$ as the first examples of spin-carrying acceptor systems while no FET property could be discerned in the corresponding naphthaleneimide derivative.

Much interest is now focused in the field of materials science on the development of organic and polymeric thin-film field effect transistors (FETs) owing to their potential applications to future electronics devices.[1] Being compared to abundant p-type FET candidates, those of n-type FET are still limited.[2]

Previously, a naphthalenediimide framework was reported to be a good candidate for n-channel FET materials,[3] and an iminonitroxide-substituted pyrene derivative was reported to exhibit p-type FET characteristics with fairly high performance, showing the significance of a radical moiety on the properties.[4] More recently, MOTFTs with radical parts have been reported to show the high-performance ambipolar FET properties.[5] These findings have prompted us to develop spin-carrying naphthalenediimide derivatives with n-type FET property as an extension of our previous work,[6] and we wish to report here the structures and magnetic as well as FET properties of a couple of naphthalenediimide derivatives carrying TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl) substituents (**2** and **3**), compared to those of the corresponding naphthaleneimide derivative **1** (Chart 1).

The naphthaleneimide and naphthalenediimide derivatives carrying TEMPO radical were prepared from naphthalene-1,8-dicarboxylic anhydride or naphthalene-1,4,5,8-tetracarboxylic dianhydride either by direct reaction with 4-amino-TEMPO or by two-step processes through the corresponding piperidine derivatives and their oxidation by MCPBA.[7] Higher yields are obtained in each case in the former (direct) method than the latter (indirect) one.

The reduction and oxidation potentials of each derivative were estimated by cyclic voltammetry, and the data are summarized in Table 1.

It is apparent from their reduction potentials that they are weak acceptors and that the diimide derivatives **2** and **3** have similar electron-accepting abilities, but still they are stronger than that of monoimide derivative **1**. Similar oxidation potentials due to the TEMPO group are observed within the three compounds but their electron-donating abilities are weakened because of the electron-withdrawing imide moiety.

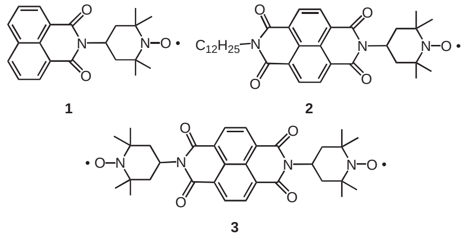

Chart 1.

Table 1. CV data of **1**–**3**[a]

Compound	E_1^{RED}	E_2^{RED}	E_1^{OX}
1	−1.01	−1.55	0.85
2	−0.78	−1.24	0.89
3	−0.75	−1.21	0.88
TEMPO			0.70

[a] V vs. SCE, 0.1 M n-Bu_4NClO_4 in dichloroethane.

The crystal structure of monoimide derivative **1** is shown in Figure 1.[8]

There are two crystallographically independent molecules in this crystal, and the TEMPO moiety is largely distorted from the π plane of naphthaleneimide in each molecule. The molecules stack along the c axis (Figure 1, left), in which the formation of dimer pair is observed and the intra- and interdimer distances are 3.62 and 3.75 Å, respectively. They form columnar structures but the π planes are oriented in a staggered manner and in addition, there is almost no interaction between the columns, i.e., they are isolated. Owing probably to the packing structure together with weak electron-accepting ability, no FET properties could be observed in this compound.

On the contrary, apparent FET properties could be found for the diimide derivatives **2** and **3** (SI-Figures 1 and 2).[9] The FET devices were fabricated on SiO_2/Si substrates by vapor deposition. Gold electrodes forming channels of 5-µm length (L) and 38-mm width (W) were photolithographically defined. The semiconductor layer (50 nm) was evaporated on the substrate surface, where the SiO_2 layer was 300 nm thick. The FET characteristics are summarized in Table 2.

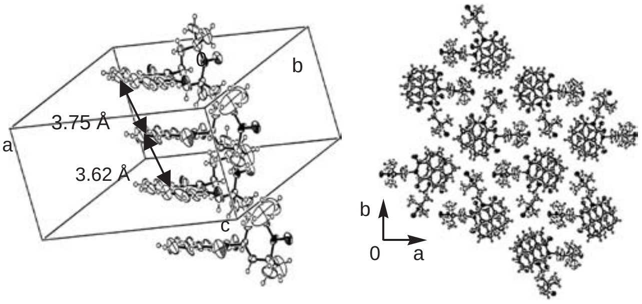

Figure 1. (left) Crystal structure of **1**. Intra- and interdimer distances are shown. (right) Crystal structure of **1** viewed along the c axis.

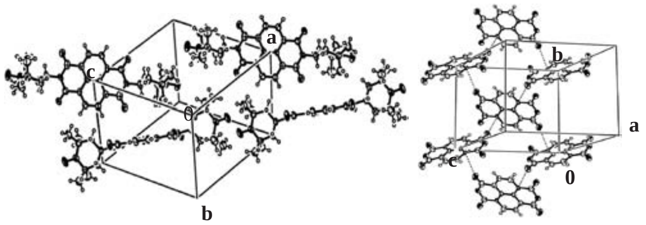

Figure 2. (left) Crystal structure of **3**. (right) Crystal structure of **3**, indicating the naphthalenediimide moiety. Several short distances between the oxygen atoms and naphthalene planes are depicted.

Table 2. Mobilities and $I_{\mathrm{on}}/I_{\mathrm{off}}$ ratios of **1** and **2**[a]

Compound	mobilities ($\mathrm{cm^2/V{\cdot}s}$)	$I_{\mathrm{on}}/I_{\mathrm{off}}$
2 (bare)	5.4×10^{-7}	40
2 (HMDS)	4.9×10^{-7}	40
3 (bare)	7.5×10^{-7}	400
3 (HMDS)	2.6×10^{-5}	310

[a]Fabricated on Au bottom electrodes, SiO_2/Si substrates, SiO_2 300 nm. [b]HMDS: hexamethyldisilazane.

The radical compound **2** showed n-type characteristics, and the electron mobility was about $5 \times 10^{-7}\,\mathrm{cm^2/V{\cdot}s}$, although the lack of a crystal structure prevents seeing its structure–property relationship in detail. On the other hand, the crystal structure of **3** could be solved, and it sheds some light on its relationship (Figure 2).

Also in this case, the TEMPO moiety is largely distorted from the π plane of naphthalenediimide, and the molecules are stacked along the *b* axis in an edge-to-face manner as shown in Figure 2 (left). Being different from the structure of **1**, there are several short contacts of ca. 3.3 Å between the molecules, in the different columns to form the pathways of 2D interactions and it may be beneficial for FET performance. Actually, the FET device based on **3** exhibited electron mobility of ca. $10^{-5}\,\mathrm{cm^2/V{\cdot}s}$ on the HMDS-treated substrates. The mobility is significantly higher than that of **2**, and the on/off value is also improved. Although the film of **3** deposited on the SiO_2/Si substrate was investigated by X-ray diffraction (XRD), no clear peak was observed (SI), and it is still ambiguous to what extent the radical parts contribute to the conduction of electron. Apparently, the suggestion in a previous paper[4] that the molecules of the first layer are arranged regularly for the hydrogen-bond interaction between NO and OH on the SiO_2 surface to facilitate the transport of the carriers is not always warranted, since the transport of the carriers for the compound **3** is facilitated when the surface is treated by HMDS (Table 2).

The magnetic data for the radical compounds **1**–**3** are summarized in Table 3.

Table 3. Magnetic data of **1**–**3**[a]

Compd.	Magnetic interaction	C[c]	θ[d]	J[e]
1	AF[a]	0.38	−0.93	—
2	AF[a]	0.38	−0.93	—
3	AF[b]	—	—	−2.59

[a]Curie–Weiss (CW) model. AF: Antiferromagnetic interaction. [b]Singlet–triplet (ST) model. [c]Curie constant ($\mathrm{emu{\cdot}K{\cdot}mol^{-1}}$). [d]Weiss temperature (K). [e]Exchange interaction (K).

Almost the same CW behaviors with weak antiferromagnetic interactions are apparently observed in the spins of the monoimide derivative **1** and the diimide derivative **2** irrespective of the difference of their FET properties, while ST behavior of weak antiferromagnetic interactions is predominantly found in the spins of diimide derivative **3**. The magnetic behavior observed in **3** can be explainable by considering relatively short O–O distance (4.04 Å) between the spin centers (SI), which may also contribute to the aggregation of the molecules in 2D manner.

Thus, whereas naphthaleneimide derivative **1** carrying a TEMPO substituent does not show any appreciable FET properties, apparent n-type FET properties are revealed in the naphthalenediimide derivatives **2** and **3** to provide the first examples of organic radical compounds exhibiting n-type FET properties on one hand and inherent paramagnetic properties on the other hand.

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8 Crystal data of **1** and **3** reported in this paper have been deposited with Cambridge Crystallographic Data Centre. Copies of the data can be obtained via www.ccdc.cam.ac.uk/conts/retrieving.html.

9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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