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Spin-Carrying Naphthalenediimide and Perylenediimide Derivatives

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A couple of naphthalenediimide **4** and **5** and series of perylenediimide derivatives **6**–**9** carrying TEMPO radical were prepared and their redox, FET, and magnetic properties were investigated. The radical compounds **4** and **6**–**9** were found to show antiferromagnetic interactions obeying the Curie–Weiss model, while the naphthalenediimide derivative **5** exhibited a singlet–triplet magnetic behavior and it could be well understood by the short oxygen-to-oxygen distance between the spin centers observed in its crystal structure. Owing presumably to their appropriate reduction potentials and structural motifs, exhibitions of n-type FET properties were disclosed in these radical compounds with mobilities of the order from 10^{-5} to $10^{-8}\,cm^2\,V^{-1}\,s^{-1}$ and apparent increase of mobilities was observed in the radical compounds **5** and **7** by the surface treatment with HMDS.

The search for new organic semi-conducting materials for field effect transistors (FET) is of increasing interest because they are expected to be promising components in future organic electronics due to their possible applications such as integrated circuits for flexible electronics.[1] So far most of the high-mobility compounds have been mainly p-type transistors and some of them show device performances comparable to those of amorphous silicon.[2]

In turn, a combination of p- and n-type FETs is required especially for applications such as complementary circuits and hence the concurrent development of organic n-type FETs is desirable. In this context, considerable efforts have also been taken in the development of organic n-type FETs,[3] although still a limited number of compounds have been proposed as n-type FET materials such as oligothiophenes with fluorinated substituents,[4] metallophthalocyanines,[5] hetero-tetracyanoquinodimethanes,[6] dicyanopyrazinoquinoxalines,[7] or anthraquinones.[8] Among them, considerable attention has been paid to naphthalenediimide[9] and perylenediimide derivatives[10] as attractive candidates for n-type FET materials.

In the course of our studies toward organic magnetic materials with multifunctional properties,[11] we have been interested in preparing organic spin systems with magnetic and possible FET properties. So far only a couple of radical compounds, a nitronylnitroxide-substituted TTF derivative with long alkyl chains **1**[12] and an iminonitroxide-substituted pyrene derivative **2** (Chart 1),[13] have been known exhibiting p-type characteristics and no radical compound exhibiting n-type characteristics has been reported. Therefore, we have intended to prepare a new class of spin-carrying naphthalenediimide and perylenediimide derivatives with possible n-type FET characteristics and TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl) radical has been selected as a spin source mainly from preparative reasons. In this paper, we wish to report the preparation of a naphthaleneimide derivative **3** and a couple of naphthalenediimide derivatives **4** and **5** together with four kinds of perylenediimide derivatives **6**–**9** carrying TEMPO radical and their magnetic as well as FET properties.[14] Although it was well anticipated that these radicals might be amphoteric compounds showing both n- and p-type FET properties, we have concentrated on examining their n-type properties based on their electron-withdrawing naphthalenediimide or perylenediimide moieties.

Results and Discussion

Preparation and Electrochemical Properties of Radical Compounds. The naphthaleneimide derivative **3** could be prepared in 37% yield directly by heating a mixture of naphthalene-1,8-dicarboxylic anhydride and 4-amino-TEMPO in *N*,*N*-dimethylacetamide (DMA) with acetic acid for several hours as shown in Scheme 1 (1). In turn, it was also available by a stepwise reaction (indirect method) of naphthalene-1,8-dicarboxylic anhydride with 4-amino-2,2,6,6-tetramethylpiperidine to give at first the corresponding piperidine derivative followed by its oxidation with MCPBA (*m*-chloroperbenzoic acid)[15] but the yield was lower (28%) than that of the direct method. Similarly, naphthalenediimide derivatives **4** and **5** could be obtained by the direct method (2) or (3) in 24% (for **4**) and 67% (for **5**) respectively by reacting naphthalene-1,4,5,8-tetracarboxylic dianhydride with 1 equiv each of 4-amino-TEMPO and dodecylamine or 2 equiv of 4-amino-TEMPO in higher yield than the corresponding indirect method such as (2′) with 12% yield.

Since the direct reaction of 3,4,9,10-perylenetetracarboxylic dianhydride with 4-amino-TEMPO did not work well probably because of the low solubility of the dianhydride in organic solvents, we tried to introduce either a long alkyl chain to the imide nitrogen or such substituents as bromine or nitrile to the

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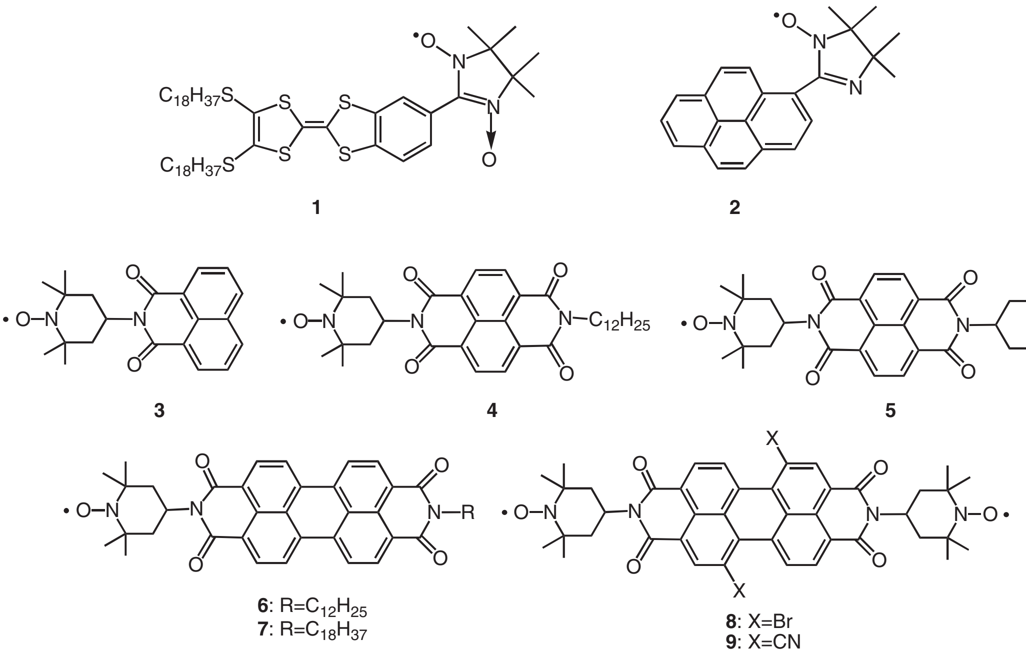
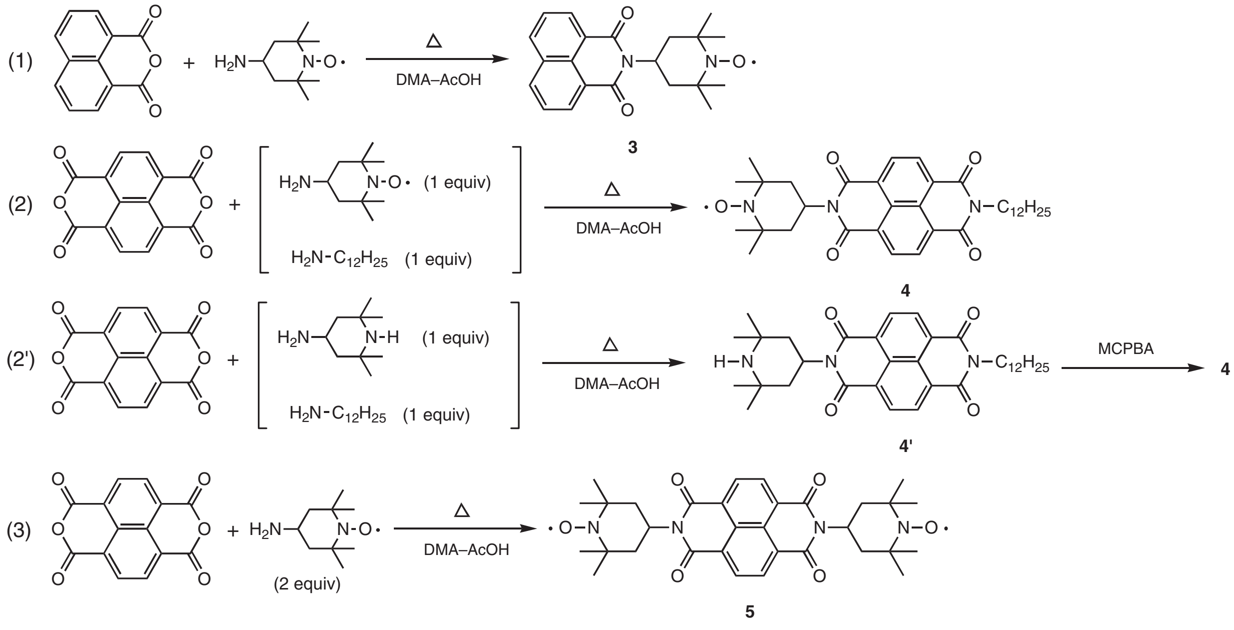


Chart 1.



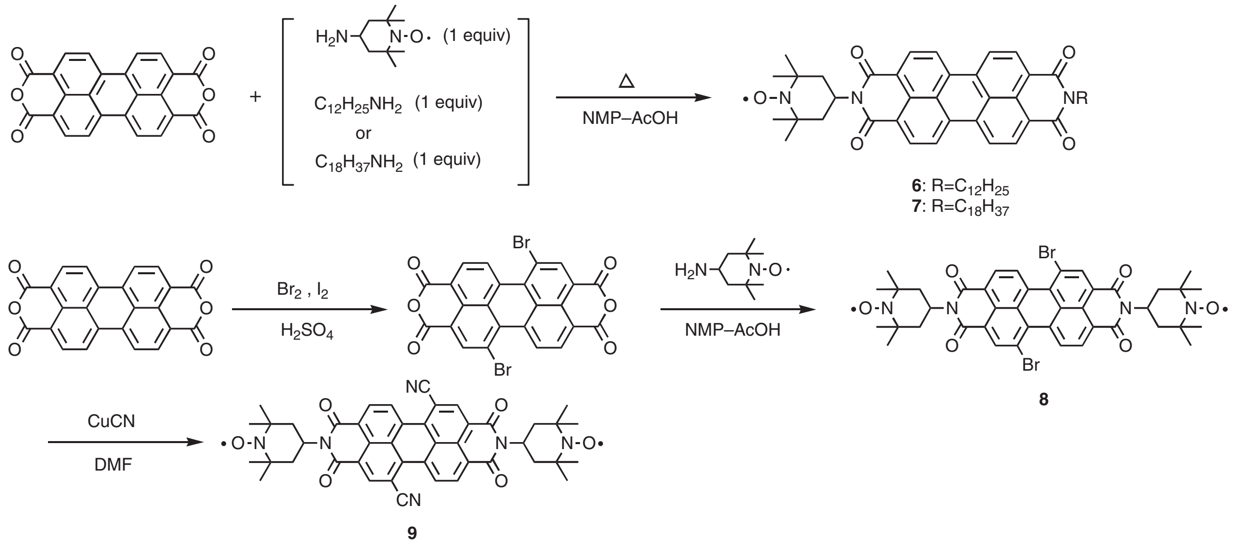
Scheme 1.

perylene core to improve its solubility. Furthermore, the introduction of a long alkyl chain was supposed to help a favorable stacking structure of the π-framework by its hydrophobic interaction and that of an electron-withdrawing group to the aromatic core was expected to be beneficial to the n-type FET property.

Similar to the naphthalenediimide derivative **4**, the reaction of the dianhydride with 1 equiv each of 4-amino-TEMPO and dodecylamine or octadecylamine gave the corresponding mono-TEMPO-substituted compounds **6** or **7**, though the yield was low (13% for **6** and 9% for **7** respectively) (Scheme 2). The reaction of the dianhydride with the mixture of bromine and iodine in sulfuric acid gave a 1,7-dibromo derivative, which could be transformed to the corresponding bis-TEMPO-substituted derivative **8** (59%) by heating with 4-amino-TEMPO in *N*-methylpyrrolidone (NMP) and acetic acid. Further reaction of **8** with copper(I) cyanide in DMF afforded 1,7-dicyano derivative **9** (36%) by replacement of the bromine atoms to nitrile groups.

In order to verify the reduction and oxidation potentials of radical compounds thus prepared, cyclic voltammetry measurements were carried out and the data are summarized in Table 1.

It is apparent from the data that they are in general weak acceptors but perylenediimide derivatives **6**–**9** are relatively



Scheme 2.

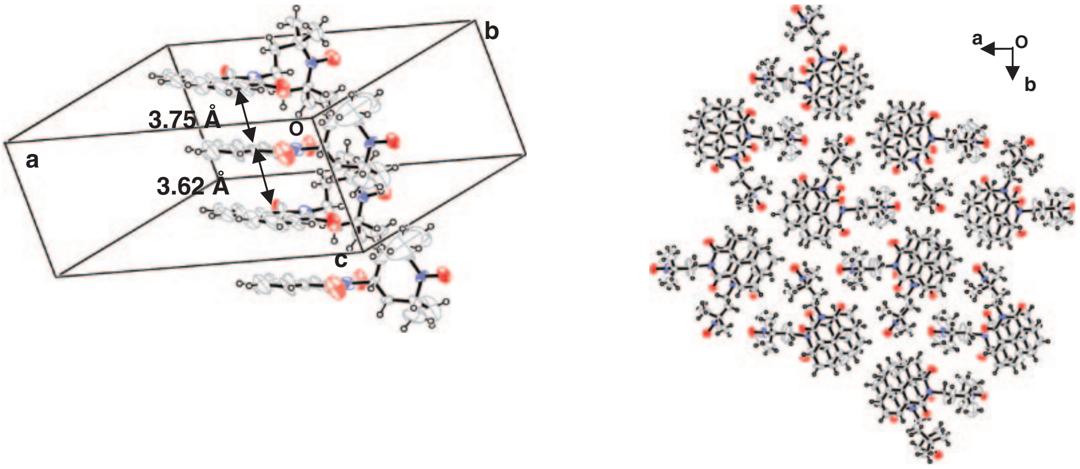


Figure 1. (left) Crystal structure of **3**. Intra- and inter-dimer distances are shown. (right) Crystal structure of **3** viewed along the *c* axis.

Table 1. CV Data of Radical Compounds[a)]

Compound	E_1^{RED}	E_2^{RED}	E_1^{OX}
3	−1.01	−1.55	0.85
4	−0.78	−1.24	0.89
5	−0.75	−1.21	0.88
6	−0.68	−0.92	0.86
7	−0.68	−0.97	0.92
8	−0.53	−0.77	0.88
9	−0.32	−0.63	0.89
TEMPO			0.70

a) V vs. SCE, 0.1 M *n*-Bu_4NClO_4 in dichloromethane for **3**–**5** and dichloroethane for **6**–**9**, scan rate: 50 mV s^{-1}.

stronger acceptors than naphthalenediimide derivatives **4** and **5** and naphthaleneimide derivative **3** is the weakest among them. Within the radical compounds, the strongest acceptor is the dicyano compound **9** due to the presence of the effective electron-withdrawing substituent. The alkyl-substituents make no large difference of the reduction potentials as seen for **4** and **5** or **8** and **9**. Similar oxidation potentials due to the TEMPO group were observed in all compounds and these values indicate that their electron-donating abilities are weakened compared to that of TEMPO itself because of the attachment of electron-withdrawing imide moiety.[16]

Crystal Structures of 1 and 3. Among the radical compounds thus prepared, single crystals suitable for X-ray analysis could be obtained only for the compounds **3** and **5** and the results of which are described. The crystal structure of naphthaleneimide derivative **3** is illustrated in Figure 1.

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 (left in Figure 1), in which the formation of dimer-pair is observed and the intra- and inter-dimer distances are 3.62 and 3.75 Å, respectively. They form columnar structures but their π-planes are oriented in a staggered manner (right in Figure 1) and in addition, there is almost no interaction between the columns, i.e., they are isolated columns.

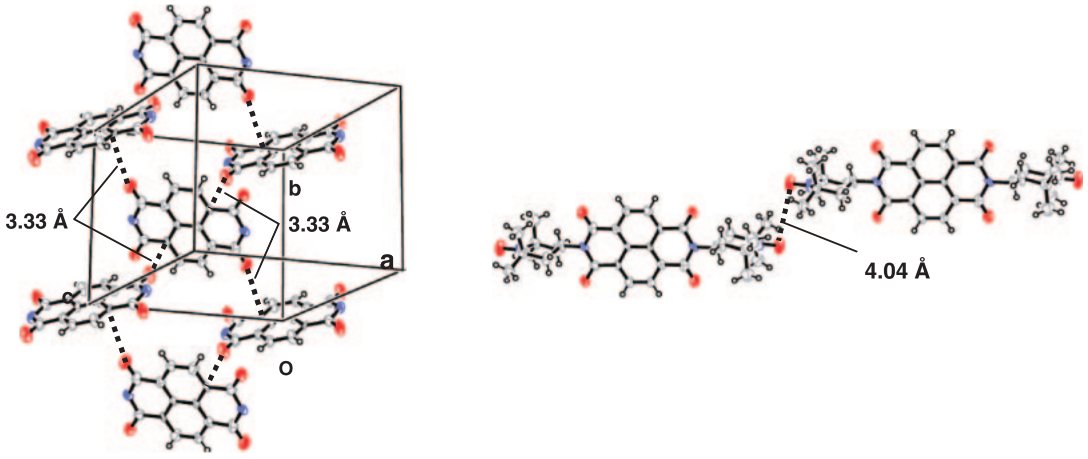


Figure 2. (left) Crystal structure of **5**, indicating only the naphthalenediimide moiety. Several short distances between the oxygen atoms and naphthalene planes are depicted in dotted lines. (right) Crystal structure of **5**, depicting two molecules and indicating short oxygen-to-oxygen contacts between them.

Table 2. Magnetic Data of Radical Compounds

Compound	Magnetic interaction	C[c] /emu K mol^{-1}	θ[d] /K	(J/k_B)[e] /K
3	antiferromagnetic[a]	0.38	−0.93	—
4	antiferromagnetic[b]	0.38	−0.93	—
5	antiferromagnetic[a]	—	—	−2.59
6	antiferromagnetic[a]	0.36	−1.27	—
7	antiferromagnetic[a]	0.37	−5.31	—
8	antiferromagnetic[a]	0.75	−0.98	—
9	antiferromagnetic[a]	0.71	−1.09	—

a) Fitting for the Curie–Weiss model. b) Singlet–triplet model. c) Curie constant. d) Weiss temperature. e) Exchange interaction.

Apparently different crystal structure from that of **3** was revealed in the naphthalenediimide derivative **5** as shown in 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). However, being different from the structure of **3**, there are several short contacts of ca. 3.3 Å between the molecules in the different columns to form the structure with 2D interactions, which may be beneficial for FET performance. Relatively short O–O distance (4.04 Å) exists between the spin centers (Figure 2, right), which may reflect the magnetic behavior of this compound (vide infra) and also contribute to the aggregation of the molecules in a 2D manner.

Magnetic Properties of Radical Compounds. The magnetic susceptibility data of the radical compounds were obtained by using a SQUID susceptometer in the temperature range of 2–300 K and the data are summarized in Table 2.

Antiferromagnetic interactions of Curie–Weiss behavior are observed in all of the radical compounds except **5** and their Curie constants are close to the theoretical values (0.375 for $S = 1/2$ spin or 0.75 for non-interacting $S = 1$ spin), indicating that the spins are alive. The magnetic interaction of **5** can be analyzed by a singlet–triplet model with a weak exchange interaction and the behavior may be understandable by taking the short O–O contact between the spin centers into consideration as seen in its crystal structure (Figure 2, right). Similar Weiss temperatures of ca. $\theta = -1$ K were found for the compounds except **7**, which shows a relatively large value due probably to an aggregated structure by hydrophobic interactions between long alkyl groups.

FET Properties of Radical Compounds. The FET devices for the compounds **3**–**5** were fabricated with bottom-contact geometry 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.

Apparently, n-type FET properties could be found for the naphthalenediimide derivatives **4** and **5** as illustrated in Figure 3, whereas no FET property could be observed in naphthaleneimide derivative **3**. The FET characteristics of the compounds **4** and **5** are summarized in Table 3.

While the radical compound **4** showed n-type characteristics and the electron mobility was about $5 \times 10^{-7}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ irrespective of the surface treatment by HMDS (hexamethyldisilazane) or non-treatment, the FET device based on **5** exhibited the electron mobility of the order of $10^{-5}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ when treated by HMDS. That is, the mobility of **5** treated by HMDS is significantly higher than that of **4** but the on/off ratios are smaller for **5** than those of **4** irrespective of the treatment. When the film of **5** deposited on the SiO_2/Si substrate was investigated by X-ray diffraction (XRD) in a bare condition, a peak at $2\theta = 5.32°$ was observed, indicating that the distance between layers is 16.59 Å (SI-1, Supporting Information). As the molecular length of **3** is estimated from the X-ray data to be ca. 18.1 Å, the slightly tilted molecules are supposed to form the first layer in the vertical direction from the surface. On the other hand, no clear peak was observed for the film of **5** treated by HMDS (SI-2) and then the packing feature of the molecules in the condition is ambiguous. Also, the stability of TEMPO spin is still unclear under this condition.

There is no large difference of the mobilities between **4** and the reference compound **4′** without the radical spin (amino derivative), even though the on/off ratios are significantly

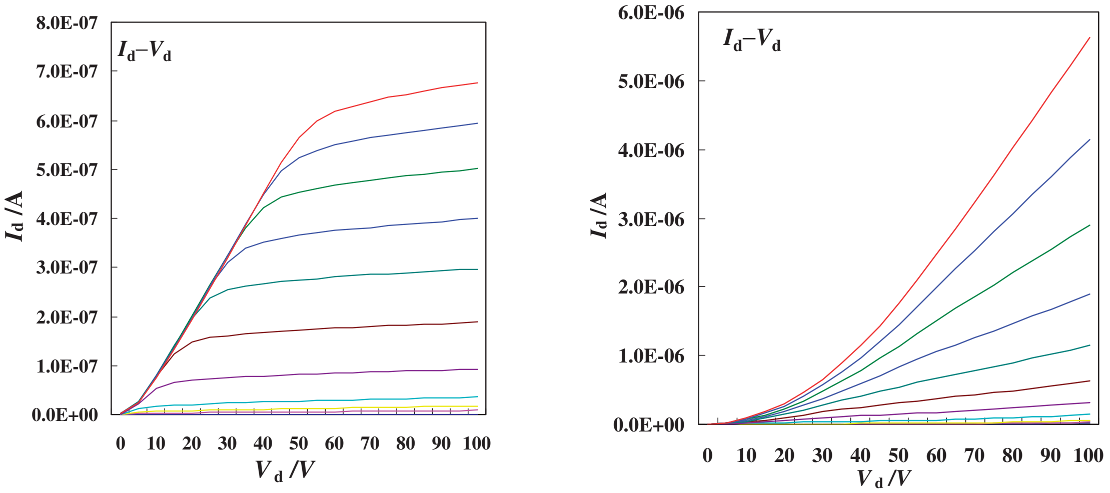


Figure 3. I_d–V_d curve of **4** (left) and **5** (right) (treated by HMDS) at room temperature. Applied gate voltages are 0 to 80 V for each device.

Table 3. Mobilities and I_{on}/I_{off} Ratios of **4** and **5**[a]

Compound	Mobilities/cm^2 V^{-1} s^{-1}	I_{on}/I_{off}
4 (bare)	5.4×10^{-7}	680[c]
4 (HMDS[b])	4.9×10^{-7}	680[c]
4′ (bare)	6.1×10^{-8}	1.4
4′ (HMDS[b])	1.4×10^{-7}	33
5 (bare)	7.5×10^{-7}	400
5 (HMDS[b])	2.6×10^{-5}	310

a) Fabricated on Au bottom electrodes, SiO$_2$/Si substrates, SiO$_2$: 300 nm. b) HMDS: hexamethyldisilazane. c) The value reported ($I_{on}/I_{off} = 40$) in Ref. 14 should be amended.

Table 4. Mobilities and I_{on}/I_{off} Ratios of **6**–**9**

Compound	Mobilities/cm^2 V^{-1} s^{-1}	I_{on}/I_{off}
6[a]	3.7×10^{-8}	37
7[a]	1.5×10^{-8}	25
7 (HMDS[b])	3.1×10^{-6}	600
8[a]	2.3×10^{-7}	97
9[a]	4.2×10^{-8}	10

a) Fabricated on Au bottom electrodes, SiO$_2$/Si substrates, SiO$_2$: 300 nm, bare condition. b) HMDS: hexamethyldisilazane.

higher for **4** and it may reflect the role of NO groups to the transport properties. However, a suggestion in a previous paper[13] 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 **5** is facilitated when the surface is treated by HMDS.

On the other hand, the FET devices of perylenediimide derivatives **6**–**9** were fabricated by a solution method because they could not be evaporated. The devices were prepared by applying a chloroform solution on the substrate, which is the same with that used for **3**–**5**, followed by annealing at 100 °C for 15 min. As summarized in Table 4, n-type FET properties could also be observed for **6**–**9** even in bare conditions (figures of I_d–V_d curves are shown in SI-3, SI-4, and SI-5).

The electron mobilities of the perylenediimide derivatives are of the order of 10^{-7}–10^{-8} cm^2 V^{-1} s^{-1} in bare conditions and the values are comparable to those of naphthalenediimide derivatives **4** and **5** in similar conditions but fairly smaller than that of *N*,*N′*-octadecylperylene derivative, which is reported to exhibit mobility as high as 0.6 cm^2 V^{-1} s^{-1}.[10b] The improvement of the mobility and on/off ratio is clarified for compound **7**, like compound **5**, when the surface is treated with HMDS.

Conclusion

A naphthaleneimide and a couple of naphthalenediimide derivatives together with four kinds of perylenediimide derivatives have been prepared and their electrochemical properties have been investigated. They are found to be amphoteric compounds having both acceptor and donor characteristics and the perylenediimide derivatives **6**–**9** are relatively stronger acceptors than the naphthalenediimide derivatives **4** and **5** or the naphthaleneimide derivative **3**.

The radical compounds are also found to exhibit antiferromagnetic interactions of Curie–Weiss behavior except **5**, which showed singlet–triplet behavior, and its behavior could be well understood by considering the short O–O distance between the spin centers observed in the crystal structure.

Whereas naphthaleneimide derivative **3** carrying a TEMPO-substituent does not show any appreciable FET property, apparent n-type FET properties are revealed in the naphthalenediimide derivatives **4** and **5** or perylenediimide derivatives **6**–**9**. The mobility of **5** after the surface treatment with HMDS is significantly higher than those of **4** as well as **6**–**9** and the improvement of the mobility is also clarified for the compound **7** with the HMDS treatment. Being different from the structure of **3**, there are several short contacts between the molecules of **5** in the different columns to form the structure with 2D interactions, which can be beneficial for FET performance as revealed in the results. The significance of the existence of a nitroxide group is reflected in relatively high on/off ratios found in **4** compared to those found in **4′** without the group.

Thus, the apparent n-type FET properties are revealed in the spin-carrying naphthalenediimide derivatives **4** and **5** as well as in the perylenediimide derivatives **6**–**9** to provide unique examples of organic multifunctional radical compounds exhibiting inherent paramagnetic properties on one hand and n-type FET properties on the other hand. Nonetheless, the synergy between these two properties still remains to be explored.

Experimental

Materials. The reagents used for the preparation of the radical compounds described in the text were commercially available and were used without further purification.

Instrumentation. Melting points were measured on a YAMATO MP-21 apparatus and are uncorrected. MS spectra were taken using a JEOL JMS-AX 505 mass spectrometer. Susceptibility measurements were carried out on a QUANTUM DESIGN MPMS-5 SQUID susceptometer, using ca. 10 mg for each powdered sample in the usual way. X-ray diffraction data were collected on a Rigaku AFC-7R diffractometer with Mo Kα radiation at room temperature and were recorded using a CCD area detector. The refinements were made by full-matrix least-squares methods. Anisotropic temperature factors were used for the non-hydrogen atoms and the hydrogen atoms were included in the final calculation. All the calculations were performed using the Crystal Structure crystallographic software package.[17] Crystal data of **3** and **5** have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-711651 for **3** and CCDC-711652 for **5**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

On the Calculation of Mobilities. Mobilities (μ) were calculated in the saturation regime by the relationship: $\mu_{\mathrm{sat}} = (2I_{\mathrm{DS}}L)/[WC_{\mathrm{ox}}(V_{\mathrm{SG}} - V_{\mathrm{th}})^2]$ where I_{DS} is the source–drain saturation current: C_{ox} is the silicon oxide capacitance per unit area of the gate dielectric. V_{SG} is the gate voltage and V_{th} is the threshold voltage. The latter can be estimated as the intercept of the linear section of the plot of V_{SG} $(I_{\mathrm{DS}})^{1/2}$. In the case of **5** and **9** having two TEMPO moieties at both terminal positions, the saturation regime was not observed in their output characteristics and then their mobilities were calculated by using I_{d} values at $V_{\mathrm{d}} = 100$ V.

Preparation of Naphthaleneimide Derivative 3. To a stirred solution of 1,8-naphthalic anhydride (1.01 g, 5.09 mmol) in DMA (20 mL) and acetic acid (1 mL) was added 4-amino-2,2,6,6-tetramethylpiperidine (1.05 g, 6.72 mmol) and the mixture was heated for 3 h at 100 °C. After concentration of the reaction mixture under reduced pressure, the resulting crude substance was purified by column chromatography (SiO_2, dichloromethane/ethanol) to give a white solid (1.57 g) of the condensed compound. Part of the substance (0.21 g) was then reacted with an excess amount of MCPBA (0.21 g, 1.20 mmol) in dichloromethane (20 mL) at room temperature for 3 h. The reaction mixture was then concentrated under reduced pressure to give a crude product, which was purified by column chromatography (Al_2O_3, dichloromethane) and recrystallization from diethyl ether/dichloromethane to give **3** as orange needles (70 mg, 28%, 2 steps). Alternatively, when 1,8-naphthalic anhydride (0.15 g, 0.76 mmol) was reacted with 4-amino-TEMPO (0.21 g, 1.2 mmol) in DMA (50 mL) and acetic acid (2 mL) for 3 h at 100 °C, 0.10 g (37%) of **3** was obtained after similar purification. Mp 214 °C; FAB-MS: m/z 352 (M + 1); Anal. Calcd for $C_{21}H_{23}N_2O_3$: C, 71.77; H, 6.60; N, 7.97%. Found: C, 71.63; H, 6.67; N, 7.86%. In a similar manner, **4** was prepared by indirect method in 12% and by direct one in 24% yield, respectively, and was obtained as pale red needles. Mp 157–158 °C; FAB-MS: 589 (M + 1); Anal. Calcd for $C_{35}H_{46}N_3O_5$: C, 71.39; H, 7.88; N, 7.14%. Found: C, 71.14; H, 8.02; N, 6.97%. Likewise, **5** was prepared by indirect method in 27% and by direct one in 67% yield, respectively, and was obtained as orange plates. Mp 240 °C; FAB-MS: 575 (M + 1); Anal. Calcd for $C_{32}H_{38}N_4O_6$: C, 66.88; H, 6.67; N, 9.75%. Found: C, 66.41; H, 6.67; N, 9.42%.

The perylenediimide derivatives **6** and **7** were prepared in *N*-methylpyrrolidone (NMP) solution by the direct method in a similar manner to the preparation of **6** in 13% and 9% yields, respectively and the analytical data are as follows: **6**: Mp 260 °C (decomp.); FAB-MS: 714 (M + 1); Anal. Calcd for $C_{45}H_{50}N_3O_5 \cdot 1.5H_2O$: C, 73.05; H, 7.22; N, 5.68%. Found: C, 73.25; H, 7.05; N, 5.39%. **7**: Mp 248 °C (decomp.); FAB-MS: 798 (M + 1); Anal. Calcd for $C_{51}H_{62}N_3O_5 \cdot H_2O$: C, 75.15; H, 7.91; N, 5.16%. Found: C, 75.51; H, 7.82; N, 5.00%.

Preparation of Perylenediimide Derivatives 8 and 9. A stirred mixture of 1,7-dibromo-3,4,9,10-perylenetetracarboxylic dianhydride[10c] (0.22 g, 0.40 mmol) and 4-amino-TEMPO (0.20 g, 1.19 mmol) in NMP (10 mL) and acetic acid (2 mL) was heated for 24 h at 90 °C. After cooling, the reaction mixture was poured into methanol (200 mL) to obtain precipitates, which were filtrated, washed with methanol and extracted with chloroform (200 mL). The chloroform layer was concentrated in vacuo and the residue was purified by column chromatography (SiO_2, dichloromethane/diethyl ether) at first and then recrystallized from chloroform/ethanol to give **8** (0.20 g, 59%) as slightly hygroscopic red needles. Mp 245 °C (decomp.); FAB-MS: 857 (M + 1); Anal. Calcd for $C_{42}H_{40}N_4O_6Br_2 \cdot H_2O$: C, 57.68; H, 4.84; N, 6.41%. Found: C, 57.19; H, 4.78; N, 6.16%. To a stirred solution of **8** (60 mg, 0.070 mmol) in DMF (5 mL) was added copper(I) cyanide (0.12 g, 1.4 mmol) and the reaction mixture was heated under nitrogen to 150 °C. After stirred for further 6 h at the same temperature, the reaction mixture was concentrated, poured into chloroform (200 mL), and the precipitates were removed. The remaining filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (SiO_2, chloroform/diethyl ether) and then recrystallized from chloroform/ethanol to give **9** (20 mg, 36%) as slightly hygroscopic dark red needles. Mp >300 °C; FAB-MS: 750 (M + 1); Anal. Calcd for $C_{44}H_{40}N_6O_6 \cdot 1.5H_2O$: C, 68.12; H, 5.59; N, 10.83%. Found: C, 68.30; H, 5.60; N, 10.63%.

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Supporting Information

XRD of compound **5** (bare and HMDS). I_{d}–V_{d} curves of compounds **6**, **7** (bare and HMDS), **8**, and **9**. These materials are available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

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