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PAPER

Organic field-effect transistors based on novel organic semiconductors containing diazaboroles[†]

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New π -conjugated systems containing a diazaborole unit have been prepared by the reaction of the corresponding boronic acids with diamines. They are nearly colorless compounds with electron-donating properties. Single crystal X-ray structure analysis of two compounds revealed their nearly planar structures and unique crystal structures. The OFET devices using the transparent organic semiconductors as an active layer have been successfully fabricated and showed good p-type FET behaviour. The FET device based on the derivative showed high air stability in spite of its high HOMO level. The film structures were investigated with XRD and AFM measurements.

1. Introduction

Organic semiconductors have recently attracted much attention for applications in organic electronics such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs) and organic photovoltaic cells (OPVCs). Although many p- and n-type organic semiconductors have already been reported, development of new materials is still important for the progress in this field.¹

On the other hand, boron is a very attractive atom since it has a vacant 2p orbital, which leads to Lewis acid characteristics and electron accepting properties. Boron-containing materials have been used for chemical sensors, electroluminescence, non-linear optics and hole or electron transporting materials.² However, compounds with tricoordinated boron atoms have not been used as semiconductors for OFETs, although some tetracoordinated boron-containing compounds exhibited FET behavior.³ This is attributed to the fact that compounds with vacant 2p orbital of boron atom are generally unstable and bulky substituents are introduced for stabilization. Such bulky groups disturb intermolecular interactions necessary for effective charge carrier transport. Therefore, we first focused on boronate esters and the related derivatives, and succeeded in fabricating OFETs based on them, although the hole mobilities are not so good.⁴ As an extension of this work, we have now focused on diazaboroles. There are many reports about diazaboroles, and their synthesis, structure, electro chemical properties and efficient fluorescence have been reported.⁵ However, the carrier transporting properties in the solid state of diazaboroles have been little studied. Diazaboroles have the following advantages as organic semiconductors. First, they can be easily prepared by a one-step reaction of boronic acids with diamino compounds. The HOMO and LUMO levels can be readily tuned by modifying the diamino compounds and boronic acids. According to Yamamoto *et al.*, diazaborole units have lower electron-donating properties than phenylenediamines, suggesting that the HOMO levels of diamines can be lowered by introducing the boron atom.⁵ Second, they are much more stable than boronate esters. Third, they have planar structures and can connect π -electronic systems. We report here the preparation, properties and structures of π -conjugated diazaboroles, and the OFETs based on them.

2. Experimental

2.1. General

Melting points were obtained on a SHIMADZU DSC-60. ¹H-NMR spectra were recorded on a JEOL JNM-ECP 300 spectrometer and referenced to the residual solvent proton resonance. EI mass spectra were collected on a JEOL JMS-700 mass spectrometer. Elemental analyses were performed at the Tokyo Institute of Technology, Chemical Resources Laboratory. UVvis spectra were recorded on a SHIMADZU MultiSpec-1500. Differential pulse voltammograms were recorded on a HOKU-TODENKO HZ-5000 containing tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 mol dm⁻³ in dry DMF). The Pt disk, Pt wire and SCE were used as working, counter, and reference electrodes, respectively. X-Ray diffraction (XRD) measurements were carried out with a JEOL JDX-3530 X-ray diffractometer system. XRD patterns were obtained using the Bragg-Brentano geometry with CuK α radiation as an X-ray

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source with an acceleration voltage of 40 kV and a beam current of 30 mA. AFM experiments for films in tapping mode were performed using an SII NanoTechnology SPA-400 (DFM) instrument.

2.2. Synthesis

Compound 1. 4.4'-Dibromobiphenvl (1.56 g, 5.0 mmol) was dissolved in anhydrous THF (70 ml), and cooled to -78 °C. tert-Butyllithium (13 ml, 20 mmol, 1.57 M in pentane) was added dropwise over 5 min to the solution. After stirring the mixture for 1 h, trimethyl borate (1.5 ml, 13.5 mmol) was added. The solution was stirred for 1 h at -78 °C and for 2 h at room temperature. The mixture was neutralized with 150 ml of 1 N HCl and extracted with diethyl ether. The organic phase was dried over Na₂SO₄, filtered and evaporated. The crude biphenyldiboronic acid was dissolved in 100 ml of toluene, and o-phenylenediamine (1.10 g, 10.2 mmol) and p-toluenesulfonic acid (one grain as a dehydration catalyst) were added to the solution. The mixture was refluxed for 24 h. The residue was filtered and sublimed to give compound 1 as an off-white solid in 40% yield (153 mg, 0.40 mmol). Mp > 400 °C. MS (EI) m/z 386 (M⁺). Anal. Calcd for C₂₄H₂₀B₂N₄: C, 74.67; H, 5.22; N, 14.51. Found: C, 74.51; H, 5.10; N, 14.39%.

Compound 2. Biphenyl-3,3',4,4'-tetraamine (535 mg, 2.5 mmol) was dissolved in 70 ml of toluene. Phenylboronic acid (1.22 g, 10.0 mmol) was added to the solution, and the mixture was refluxed for 2 d, and the residue was filtered and sublimed to give **2** as a colorless solid in 83% yield (803 mg, 2.1 mmol). Mp 338–341 °C. MS (EI) *m/z* 386 (M⁺). Anal. Calcd for C₂₄H₂₀B₂N₄: C, 74.67; H, 5.22; N, 14.51. Found: C, 74.78; H, 4.95; N, 14.52%.

Compound 3. Biphenyl-3,3',4,4'-tetraamine (428 mg, 2.0 mmol) was dissolved in 100 ml of toluene. Naphthalene-2-ylboronic acid (1.07 g, 6.0 mmol) was added to the solution, and the mixture was refluxed for 2 d, and the residue was filtered and sublimed to give **3** as a colorless solid in 25% yield (242 mg, 0.5 mmol). Mp 360–363 °C. HR-MS m/z (M⁺). Anal. Calcd for $C_{32}H_{24}B_2N_4$ 486.2187. Found 486.2188.

Compound 4. Biphenyl-3,3',4,4'-tetraamine (857 mg, 4.0 mmol) was dissolved in 50 ml of toluene. 4-Biphenylboronic acid (1.84 g, 9.3 mmol) was added to the solution, and the mixture was refluxed for 2 d, and the residue was filtered and sublimed to give 4 as a pale yellow solid in 41% yield (878 mg, 1.6 mmol). Mp > 400 °C. MS (EI) *m*/*z* 538 (M⁺). Anal. Calcd for C₃₆H₂₈B₂N₄: C, 80.33; H, 5.24; N, 10.41. Found: C, 80.28; H, 5.14; N, 10.43%.

Compound 5. A mixture of 4-phenylboronic acid (370 mg, 3.1 mmol), 1,2,4,5-tetraaminobenzene tetrahydrochloride (285 mg, 1.0 mmol) and sodium hydrogen carbonate (257 mg, 3.1 mmol) in 70 ml of toluene was refluxed for 1 d through a Soxhlet extractor containing magnesium sulfate under Ar. A pale purple solid (407 mg) was filtered and washed with hexane. Purification by sublimation gave 5 as a yellow solid (92 mg) in 30% yield. Mp > 360 °C (decomp.). ¹H NMR (300 MHz, DMSO-d₆): δ 8.70 (s, 4H, NH), 7.84 (d, *J* = 6.0 Hz, 4H, arom. H), 7.46–7.30 (m, 6H, arom. H), 6.82 (s, 2H, arom. H). MS (EI) *m/z* 310 (M⁺, 100).

Anal. Calcd. for $C_{18}H_{16}B_2N_4$: C, 69.75; H, 5.20; N, 18.08. Found: C, 69.75; H, 5.51; N, 18.20%. HR-MS/FAB *m*/*z* Calcd for $C_{18}H_{16}B_2N_4$ 310.1561. Found 310.1552.

Compound 6. 4-Biphenylboronic acid (1.27 g, 6.4 mmol) was dissolved in 50 ml of toluene. 1,2,4,5-Tetraaminobenzene tetrahydrochloride (458 mg, 1.6 mmol) was added to the solution, and the mixture was refluxed for 2 d, and the residue was filtered and sublimed to give **6** as a yellow solid in 8% yield (57 mg, 0.12 mmol). mp > 400 °C. HR-MS m/z (M⁺). Anal. Calcd for C₃₀H₂₄B₂N₄ 462.2187. Found 462.2196.

2.3. X-Ray analysis

The X-ray measurements of boronate esters 2 and 4 were carried out on a Rigaku RAXIS-RAPID Imaging Plate diffractometer (Mo-K α radiation, ($\lambda = 0.71075$ Å)). The data were collected at 93 K and the structure was solved by the direct method and refined by the full matrix least-squares method on F2 with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms of 2 and 4 were placed in geometrically calculated positions. The absorption correction was applied using the empirical procedure. All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-97.

Compound 2. $C_{24}H_{20}B_2N_4$, M = 386.07, triclinic $P\overline{1}$, a = 9.3960(7), b = 9.7337(7), c = 22.0591(15) Å, $\alpha = 78.68(2)$, $\beta = 78.5522(18)$, $\gamma = 75.835(2)^{\circ}$, V = 1893(9) Å³, Z = 4, $2\theta_{max} = 55.0^{\circ}$, $D_{calcd} = 1.354$ g cm⁻³, F(000) = 808.00, $\mu = 0.803$ cm⁻¹, 18728 reflections collected, 8631 independent ($R_{int} = 0.1736$), $R_1 = 0.0707$, w $R_2 = 0.2296$. The CCDC reference number is 767653.

Compound 4. $C_{36}H_{28}B_2N_4$, M = 538.26, orthorhombic $P2_1/n$, a = 8.6051(4), b = 5.5304(2), c = 27.6946(11) Å, $\beta = 97.8185$ (16)°, V = 1305.72(9) Å³, Z = 2, $2\theta_{max} = 55.0^{\circ}$, $D_{calcd} = 1.369$ g cm⁻³, F(000) = 564.00, $\mu = 0.801$ cm⁻¹, 12 115 reflections collected, 2992 independent ($R_{int} = 0.0480$), $R_1 = 0.0427$, w $R_2 = 0.1227$. The CCDC reference number is 767654.

2.4. Fabricating of OFETs

Bottom-contact OFETs were constructed on the heavily doped n-type silicon wafer covered with 300 nm thick thermally grown silicon dioxide. The silicon dioxide acts as a gate dielectric layer and the silicon wafer serves as a gate electrode. Cr (10 nm)/Au (20 nm) were successively evaporated and photolithographically delineated to obtain the source and drain electrodes. The channel length and width (*L/W*) were 25 μ m/6 × 49 nm, respectively. Organic thin films (50 nm) were deposited on the SiO₂ treated with HMDS (hexamethyldisilazane) or bare substrates at different substrate temperatures by vacuum evaporation (10⁻⁵ Pa). The FET measurements were carried out at room temperature in a high vacuum chamber and ambient condition.

Top-contact OFETs were constructed on heavily doped n-type silicon wafers covered with 200 nm thick thermally grown silicon dioxide. The silicon dioxide acts as a gate dielectric layer, and the silicon wafer serves as a gate electrode. Organic compounds were deposited on the SiO_2 treated with HMDS

(hexamethyldisilazane) or OTS (octyltrichlorosilane) by vacuum evaporation at a rate of 0.2–0.4 Å s⁻¹ under pressure of 10^{-4} Pa. The thickness of the semiconductor layer was 50 nm. During the evaporation, the temperature of the substrate was maintained at 80 °C by heating a copper block on which the substrate was mounted. Gold was used as source and drain electrodes and deposited on the organic semiconductor layer through a shadow mask with a channel width (*W*) of 1000 µm and a channel length (*L*) of 50 µm.

The FET measurements were carried out at room temperature in a vacuum chamber (10^{-5} Pa) without exposure to air with Hewlett-Packard 4140A and 4140B models.

Carrier mobilities (μ) were calculated in the saturation region by the relationship: $\mu_{sat} = (2I_dL)/[WC_{ox}(V_g - V_{th})^2]$, where I_d is the source–drain saturation current, C_{ox} is the oxide capacitance, V_g 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 $V_g(I_d)^{1/2}$.

3. Results and discussion

3.1. Synthesis and characterization

The syntheses of compounds 1-6 are described in Scheme 1. A convenient one-step reaction of the corresponding boronic acids with diamines and tetraamines gave the diazaboroles in approximately 25–40% yields, with the exception of 2 (83%), and 6 (6%). All of them were thermally stable and purified by sublimation. The structures were determined by the spectral data along with elemental analysis or high resolution mass spectrometry.

3.2. Optical and electrochemical properties

The optical and electrochemical properties of **1–6** are summarized in Table 1. The absorption spectra of **1–6** in solution are shown in Fig. 1. It should be noted that compounds **1–4** have no absorptions in the visible region. The absorptions of **5** and **6** are a little red-shifted compared to those of **1–4**. The spectra of **1–6** in solution are red-shifted compared to those in the solid. In this case, DMF was used for the measurement of the PL spectra. The red-shifts may be attributed to the solvent DMF, which stabilizes the polar excited states.

The differential pulse voltammograms (DPVs) of 1 exhibited the oxidation potentials at +0.88 V vs. SCE, while those of 2–4



Scheme 1 Synthesis of diazaboroles.

were +0.62, +0.64 and +0.61 V vs. SCE, respectively. The effect of end-capped aryl groups on the oxidation potentials was little. Compounds **5** and **6** were oxidized more easily than the others, because tetraaminobenzene has a higher HOMO level (-3.27 eV)than those of *o*-phenylenediamine (-4.47 eV) and diaminobenzidine (-4.51 eV), which were estimated by DFT calculations.⁶ The HOMO levels of **5** and **6** estimated from the oxidation potentials were 4.5 eV.

3.3. X-Ray single crystal analysis

The single crystals of 2 and 4 suitable for the X-ray structure analysis were obtained by sublimation. The crystallographic parameters of 2 and 4 are shown in Table 2 and these ORTEP and packing structures are shown in Fig. 2 and 3. The X-ray analysis reveals their nearly planar molecular structures. In crystal 2, there exist two crystallographically independent molecules (molecules 1 and 2). In molecule 1, the dihedral angles between the phenylene rings (C7-C12), (C19-C24) and the neighboring benzodiazaborole rings are 6.3° and 5.2°, respectively, and that of the bisbenzodiazaborole core is 8.8°. In molecule 2, the dihedral angles between the phenylene rings (C31–C36), (C43–C48) and the neighboring heterocycle are 11.8° and 4.4°, respectively, and the bisdiazaborole core is twisted by only 5.4°. These molecules are packed in a half-slipped herringbone manner. The molecule of 4 is also almost planar as expected. These molecules are also packed in a half-slipped herringbone manner. Packing of these molecules in the crystal is similar to 2. The dihedral angle between the phenylene rings (C7-C12, C13–C18) is 4.1° and that between the phenylene and the diazaborole rings is 3.2° . Interestingly, the molecules 2 and 4 have many short atomic contacts with the neighboring molecules in the crystals. In addition to the CH $-\pi$ interactions, the contacts between the boron atoms and neighboring atoms exist, which seem to be favorable to charge carrier transport.

3.4. OFET characteristics

The FET measurements were carried out at room temperature in a high vacuum chamber and ambient condition. The devices of 1 did not exhibit typical FET characteristics (Fig. 4). Instead, these devices were found to have different conductive states (high and low conductive states), and they showed unusual varistor-like I-V curves. Thus, the source-drain current comes to flow suddenly when the source-drain voltage reaches to a certain threshold voltage. The resistance values of these devices could be measured by a digital multimeter ($\sim M\Omega$). It seems that the high conductive state is produced by accumulation of the electric charge in the thin film when high voltage is applied without flowing the current between the electrodes. This phenomenon may have been caused by the electron acceptability of boron atom with vacant 2p orbital. Although this high conductive state was kept in a high vacuum, it disappeared in ambient conditions. This fact suggests that the doped state is unstable in air. Additionally, these phenomena are observed in the similar device using some dioxaborole derivatives as active layers.³ The detail is still puzzling and under investigation. On the other hand, the devices of 2-6 exhibited good p-type FET behavior. The transfer and output characteristics of 2-6 are shown in Fig. 5 and S2-S6[†],

Compound	Solution ^a		Solid			
	λ_{abs}/nm	$\lambda_{\rm em}/\rm nm$	$\lambda_{\rm em}/\rm nm$	$E_{ m ox}{}^b/ m V$	$E_{\rm red}^{b}/{\rm V}$	
1	326	445	410, 434	+0.88	_	
2	320	392	382	+0.62	_	
3	330, 339	490	417	+0.64		
4	339	481, 517	428, 444	+0.61		
5	355	437		+0.19, +1.21		
6	377	532	466, 486, 550, 599	+0.20		

Table 1 Optical properties and redox potentials of 1-6

^a In DMF. ^b In DMF 0.1 M n-Bu₄NPF₆, Pt electrode, vs. SCE.



Fig. 1 UV-vis absorptions of 1–6 in DMF.

Table 2Crystallographic parameters of 2 and 4

	Compound 2	Compound 4	
Formula	$C_{24}H_{20}B_2N_4$	$C_{36}H_{28}B_2N_4$	
Habit	Colorless needle	Colorless needle	
Space group	$P\bar{1}$	$P2_1/n$	
Crystal system	Orthorhombic	Orthorhombic	
a/Å	9.3960(7)	8.6051(4)	
b/Å	9.7337(7)	5.5304(2)	
c/Å	22.0591(15)	27.6946(11)	
α/deg	78.68(2)		
β/deg	78.5522(18)	97.8185(16)	
γ/deg	75.835(2)		
V/Å ³	1893.9(2)	1305.72(9)	
Z	4	2	
$D_{\rm calad}/g~{\rm cm}^{-3}$	1.354	1.369	
μ (Mo-K α)/cm	0.803	0.801	
No. of reflections	8631	2992	
R ₁	0.0707	0.0427	
R_{ω}	0.2296	0.1227	

and the hole mobilities, on/off ratios and threshold voltages are summarized in Table 3. All of the devices showed the improved FET performances by using the HMDS treated SiO₂/Si substrate. The performance of the device of **4** was further improved by increasing the substrate temperature. The hole mobility and on/off ratio of **2** deposited on the HMDS treated substrate at 80 °C increased compared to those fabricated at rt although the threshold voltage was little changed. The devices of **5** and **6** also showed good p-type FET behavior. Additionally, the device of **6** exhibited good FET performance in ambient conditions even 20 d later, whereas the FET performance of **5**



Fig. 2 X-Ray structure of **2**: (a) ORTEP drawing of the molecular structure, (b) molecular arrangement along the *a*-axis and (c) packing view.



Fig. 3 X-Ray structure of **4**: (a) ORTEP drawing of the molecular structure, (b) molecular arrangement and (c) packing view.



Fig. 4 Varistor like I-V property of the device based on 1.



Fig. 5 Output and transfer characteristics of the FET devices of 6 on the HMDS treated substrate at 80 $^{\circ}$ C (a) and the device of (a) in ambient condition after standing in air for 20 d (b).

Table 3 Field-effect characteristics on bottom-contact geometry^a

Compound	SiO ₂ treatment	$T_{\rm sub}/^{\circ}{\rm C}$	$\begin{array}{c} \mbox{Mobility/} \\ \mbox{cm}^2 \ \mbox{V}^{-1} \ \mbox{s}^{-1} \end{array}$	On/off ratio	Threshold/V
2	HMDS	rt	1.9×10^{-3}	5×10^4	-27
	Bare	80	1.1×10^{-4}	3×10^4	-14
	HMDS	80	5.4×10^{-3}	1×10^{5}	-25
3	Bare	rt	4.9×10^{-5}	7×10^3	-28
	HMDS	rt	2.8×10^{-4}	7×10^4	-45
4	Bare	rt	8.8×10^{-7}	1×10^2	-29
	HMDS	rt	5.5×10^{-5}	6×10^3	-43
	Bare	80	$1.5 imes 10^{-4}$	1×10^4	-20
	HMDS	80	4.5×10^{-3}	5×10^4	-26
5	Bare	rt	2.3×10^{-5}	8×10^3	-59
	HMDS	rt	1.0×10^{-3}	3×10^4	-43
	Bare	80	3.8×10^{-5}	4×10^3	-55
	HMDS	80	1.1×10^{-3}	2×10^4	-41
6	Bare	rt	$1.3 imes 10^{-3}$	7×10^4	-31
	HMDS	rt	3.2×10^{-3}	2×10^5	-39
	Bare	80	1.2×10^{-3}	4×10^4	-37
	HMDS	80	3.9×10^{-3}	1×10^5	-46

 a Electrode : Cr/Au = 10/20 nm, SiO₂/Si substrate, SiO₂: 300 nm, L/W = 25/294000 μm .

Compound	Condition	$\frac{Mobility/cm^2}{V^{-1} \ s^{-1}}$	On/off ratio	Threshold/V
6	Vacuum In air, 10 min In air, 4 d In air, 20 d	$\begin{array}{l} 3.9 \times 10^{-3} \\ 1.5 \times 10^{-3} \\ 6.2 \times 10^{-4} \\ 1.1 \times 10^{-3} \end{array}$	$\begin{array}{c} 1.3 \times 10^{5} \\ 4.4 \times 10^{4} \\ 9.1 \times 10^{5} \\ 2.3 \times 10^{5} \end{array}$	-46 -45 -30 -33

 a Electrode : Cr/Au = 10/20 nm, SiO_/Si HMDS treated substrate, SiO_2: 300 nm, $L/W=25/294000~\mu m.$

 Table 5
 Field-effect characteristics on top-contact geometry^a

Compound	SiO ₂ treatment	$T_{\rm sub}/^{\circ}{\rm C}$	$\frac{Mobility/cm^2}{V^{-1} \ s^{-1}}$	On/off ratio	Threshold/V
2 6	HMDS OTS HMDS	80 80 80	$\begin{array}{c} 1.4 \times 10^{-2} \\ 1.4 \times 10^{-2} \\ 2.8 \times 10^{-3} \\ 1.5 \times 10^{-3} \end{array}$	10^{5} 10^{5} 10^{4}	-44 -60 -28

 a Electrode : Au = 50 nm, SiO₂/Si substrate, SiO₂: 200 nm, $L/W = 50/1000 \ \mu m.$



Fig. 6 Output and transfer characteristics of top-contact devices of 2 deposited on the HMDS treated SiO₂ at 80 $^{\circ}$ C (a) and the OTS treated SiO₂ at 80 $^{\circ}$ C (b).

became dropped in a minute in the same conditions (Table 4). For the air-stability in OFETs, the HOMO levels should be lower than the energy level of electrode (5.1 eV). Therefore, it is unusual that the device of 6, which has a high HOMO level of 4.5 eV, showed good air stability.

To investigate the effect of the device structures on the FET characteristics, the top-contact devices using 2 and 6 were fabricated. The FET characteristics of 2 and 6 are summarized in Table 5, and the transfer and output characteristics of 2 and 6 deposited on the OTS or HMDS treated SiO₂ are shown in Fig. 6 and 7. The hole mobility of 2 was improved up to 1.4×10^{-2} cm² V⁻¹ s⁻¹, while the FET performance of the device of 6 was similar to that of the bottom-contact device. The device based on 6 was deteriorated in a minute on standing in air in contrast to the



Fig. 7 Output and transfer characteristics of top-contact devices of 6 deposited on the HMDS treated SiO₂ at 80 °C (a) and the OTS treated SiO₂ at 80 °C (b).

air-stable behavior observed in the bottom-contact device. This fact suggests that the air-stability of the device of 6 is due to the dense packing of molecules which protect the contact with air.

3.5. X-Ray diffractogram and AFM measurements

The organic thin films of **2**, **5** and **6** deposited on the bare or HMDS treated SiO₂/Si substrates at different temperatures were investigated by X-ray diffraction (XRD) in reflection mode and atomic force microscope (AFM). The first reflection peak observed in the film of **2** deposited on the HMDS treated substrate was $2\theta = 4.22^{\circ}$ (*d*-spacing = 2.09 nm). Since the molecular length is 2.12 nm, the molecules are considered to be arranged nearly perpendicularly to the substrate. The AFM image of the film deposited on the HMDS treated substrate at room temperature showed a large grain which is estimated to be 0.2–0.4 µm and



Fig. 8 X-Ray diffraction patterns for the film of **2** deposited on the HMDS treated SiO_2 at rt (a), the bare SiO_2 at 80 °C (b) and the HMDS treated SiO_2 at 80 °C (c) and the AFM image for the film of **2** deposited on the HMDS treated SiO_2 at rt (d).



Fig. 9 X-Ray diffraction patterns for the film of **5** deposited on the bare SiO_2 at rt (a), the bare SiO_2 at 80 °C (b), the HMDS treated SiO_2 at rt (c) and the HMDS treated SiO_2 at 80 °C (d).



Fig. 10 X-Ray diffraction patterns for the film of **6** deposited on the bare SiO₂ at rt (a), the bare SiO₂ at 80 °C (b), the HMDS treated SiO₂ at rt (c) and the HMDS treated SiO₂ at 80 °C (d).

a lamella structure (Fig. 8). In the case of the thin film of 5, the first reflection peak was observed clearly at $2\theta = 4.86^{\circ}$ (d-spacing = 1.82 nm), indicating the high crystallinity (Fig. 9). Since the molecular length estimated from the MOPAC PM6 calculations is 1.76 nm, the molecules stand on the substrate perpendicularly. In the case of the thin film of 6, the first reflection peak was observed at $2\theta = 3.76^{\circ}$ (d-spacing = 2.34 nm) (Fig. 10). However, the peaks were not clear, suggesting that the crystallinity of thin films of 6 is not so high. This may be ascribed to the fact that the biphenyl unit of the molecule is twisted because of the H-H repulsion between the phenylene rings. Since the molecular length estimated from the MOPAC PM6 calculations is 2.62 nm, the molecules are considered to be a little tilted to the substrate. The AFM measurement shows many small grains in the films (Fig. 11). The grain size of 6in the film became larger at higher temperatures and the grains are densely packed. The biphenyl unit may play an important role in the dense packing which leads to the good air stability in the bottom-contact device.



Fig. 11 AFM images for the films of **6** deposited on the bare SiO₂ at rt (a), the bare SiO₂ at 80 °C (b), the HMDS treated SiO₂ at rt (c) and the HMDS treated SiO₂ at 80 °C (d).

4. Conclusions

We developed new π -conjugated systems containing diazaborole rings **1–6** and succeeded in fabricating the FET devices based on them. Compounds **2–6** showed good p-type semiconducting behavior with hole mobilities ranging from 10^{-7} to 10^{-2} cm² V⁻¹ s⁻¹, whereas **1** showed unusual varistor-like *I–V* curve. Although compound **6** has a high HOMO level (4.5 eV), the bottomcontact devices of **6** showed good air-stability. The film of **6** is composed of densely packed grains, which was revealed by the AFM measurement. This fact suggests that the morphology of the film is strongly related to the air stability. Diazaborole derivatives have no absorptions in the visible region, leading to transparent semiconductors. These results indicate that such diazaborole derivatives are promising candidates for unique organic semiconductors.

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