COMMUNICATION www.rsc.org/chemcomm | ChemComm

Anthraquinone derivatives affording n-type organic thin film transistors†

Masashi Mamada,[a] Jun-ichi Nishida,[a] Shizuo Tokito[b] and Yoshiro Yamashita*[a]

Received (in Cambridge, UK) 17th November 2008, Accepted 9th February 2009
First published as an Advance Article on the web 26th February 2009
DOI: 10.1039/b820520e

New anthraquinone derivatives were prepared and used as active layers of organic field-effect transistors (OFETs); these devices showed good n-type characteristics and the quinones were found to be useful for organic semiconductors in OFETs.

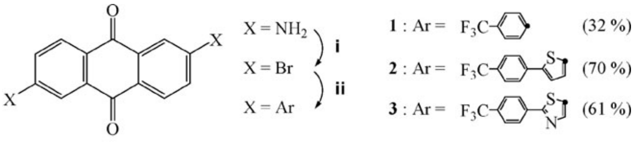
Organic field-effect transistors (OFETs) are expected to be critical components in future organic electronics, owing to their possible applications such as integrated circuits for flexible electronics.[1] In this field, many p-type organic semiconductors have been developed and their device performances are comparable to those of amorphous silicon.[2] Considerable efforts have also been taken in the development of n-type OFETs.[3] Perylenediimide derivatives are well-known as n-type materials that afford high performance OFET characteristics,[4] and some other carbonyl-compounds have also been used as OFETs in recent years.[5] However, quinones have attracted little attention as organic semiconductors for OFETs. Although an acene quinone has shown p-type characteristics, n-type behavior of quinones has not been reported.[6] Quinones have a high electron affinity and various kinds of derivatives are known. Their preparation is relatively easy and in addition, it is possible to control the molecular arrangement by hydrogen bonding through the carbonyl groups. Therefore, we have now designed anthraquinone (AQ) derivatives **1–3** to evaluate the potential of quinones as n-type semiconductors. Trifluoromethylphenyl groups were introduced as end substituents in them because they effectively induce n-type behavior.[7]

Scheme 1 shows the synthesis of anthraquinones **1–3**. These compounds were prepared more easily than a related anthracene derivative, which was reported as an n-type semiconductor.[8] The compounds were purified by sublimation, and characterized by MS, single crystal X-ray analysis and elemental analysis.

Differential scanning calorimetry (DSC) measurements of **1–3** exhibited sharp melting peaks at 320, 347 and 379 °C, respectively, and absorption maxima were observed at 278, 364 and 349 nm in dichloromethane, which were red-shifted with extension of the π-system. Similarly, the absorption edges were more red-shifted in **2** and **3** than in **1**, suggesting smaller HOMO–LUMO energy gaps. In the films, the absorption maxima of **1–3** were observed at 318, 372 and 346 nm, respectively. The reduction potentials were measured by differential pulse voltammetry (DPV), and although the reduction peak of **1** was observed at −0.88 V *vs.* SCE, those of **2** and **3** were not obvious due to their low solubilities. The LUMO levels of **1–3**, calculated by B3LYP/6-311G(d), were −3.31, −3.25 and −3.43 eV, respectively. This fact shows that the thiazole ring has a small effect on the LUMO levels.

Single crystals of **1–3** were obtained by sublimation and X-ray structure analyses were carried out (Fig. 1).‡ The molecules of **2** and **3** were almost planar and the dihedral angles between the component rings were 1.2–2.9° in **2** and 3.1–6.3° in **3**. In contrast, the molecule of **1** was more twisted, with dihedral angles of 33.8–41.8°. Fig. 1 displays the packing structures of **1–3**, which exhibit π–π stacking. This is in sharp contrast with the herringbone structure of the related anthracene derivative.[8] The intermolecular distances in the columns were *ca.* 3.58 Å between the anthraquinone rings in **1**, *ca.* 3.45 Å between the thiophene and anthraquinone rings in **2**, and *ca.* 3.39 Å between the thiazole and anthraquinone rings in **3**. This result suggests that the intermolecular interactions along the stacking direction are smaller in **1** than in **2** and **3**. These compounds also have intermolecular interactions along the horizontal direction through quinone–benzene hydrogen contact.

Fig. 2 shows X-ray diffractograms (XRD) of the thin films of **1–3**. The XRD patterns were independent of the preparation conditions and were not consistent with the simulated patterns based on the single-crystal structures. Therefore, the thin film structures are considered to be different from those of single crystals. The reflection peak corresponding to the molecular arrangement perpendicularly standing on the substrate was observed only in **3**, but was very weak. Other reflection peaks were observed at higher 2θ with low intensities but the interpretation of the peaks is still puzzling.



(**i**) $CuBr_2$, *t*-BuNO; (**ii**) $ArB(OH)_2$ for **1**, $ArSnBu_3$ for **2** and **3**, $Pd(PPh_3)_4$

Scheme 1 The synthesis of AQ derivatives.

Fig. 3 shows tapping mode atomic-force microscopy (AFM) images of thin films of **1–3**. The film of **1** consists of layers of large grains with a flat surface, while on the other hand, the films of **2** and **3** are composed of smaller grains. Although the

---

[a] *Tokyo Institute of Technology, Interdisciplinary Graduate School of Science and Engineering, Department of Electronic Chemistry, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan. E-mail: yoshiro@echem.titech.ac.jp; Fax: +81 45-924-5489; Tel: +81 45-924-5571*

[b] *NHK Science & Technical Research Laboratories, 1-10-11 Kinuta, Setagaya-ku, Tokyo 157-8510, Japan*

† Electronic supplementary information (ESI) available: Synthesis, absorption spectra, DPV, DFT calculations and X-ray crystallographic data for **1–3**, XRD pattern of the film, AFM measurement of the film, and FET data for the bottom and top contact devices. CCDC 709632–709634. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/b820520e

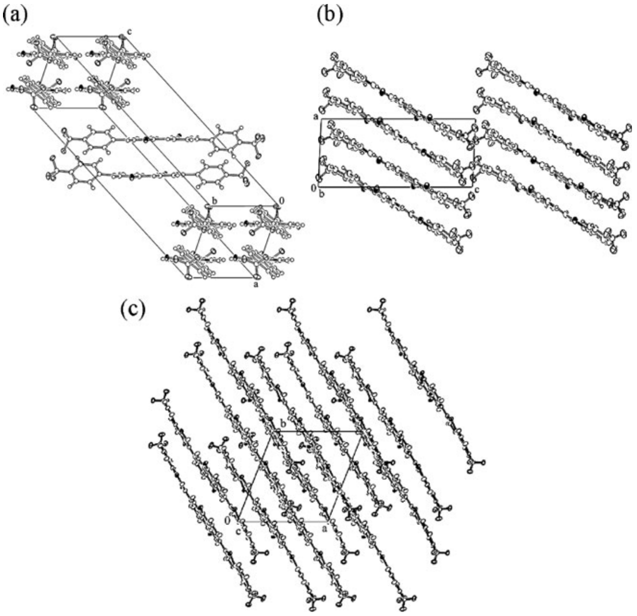


Fig. 1 (a) View of packing as seen down the long molecular axis in **1**. (b) Packing structure of **2** along the *b*-axis. (c) Packing structure of **3** along the *c*-axis.

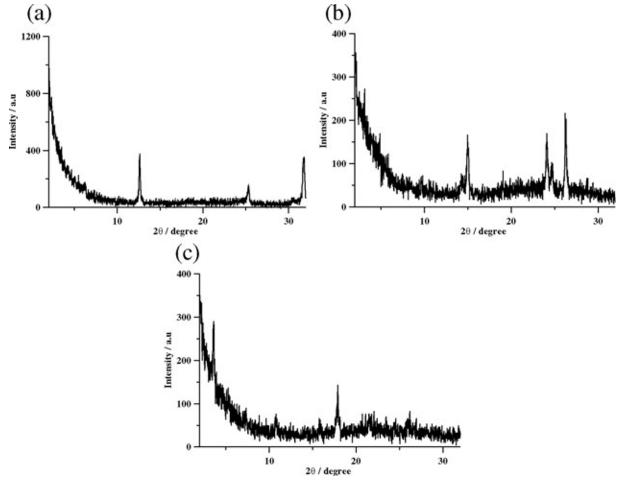


Fig. 2 X-Ray diffractograms of 50 nm films of (a) **1**, (b) **2** and (c) **3** deposited on HMDS-treated SiO_2 at 50 °C.

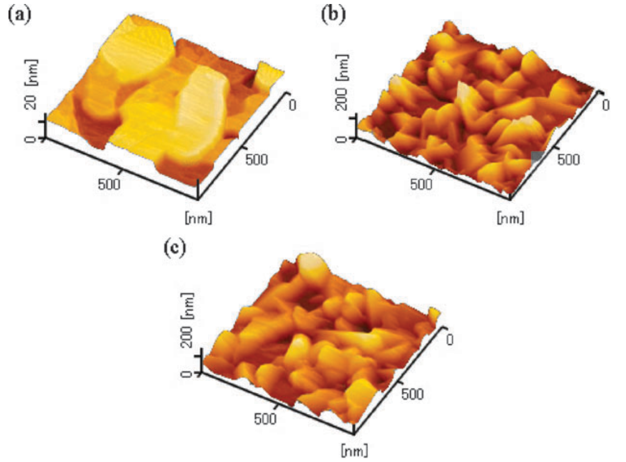


Fig. 3 The surface morphologies of 50 nm films of (a) **1**, (b) **2** and (c) **3** deposited on HMDS-treated SiO_2 at 50 °C.

Table 1 The FET characteristics of devices based on **1–3**

Compound	Contact	Mobility/ $cm^2\ V^{-1}\ s^{-1}$	On : off ratio	Threshold/V
1	Bottom[a]	7.0×10^{-4}	7×10^4	37
	Top[b]	1.2×10^{-4}	2×10^2	32
2	Bottom[c]	0.020	6×10^2	26
	Top[b]	0.005	1×10^4	26
3	Bottom[c]	0.074	1×10^4	25
	Top[b]	0.067	3×10^5	21

[a] SiO_2: 300 nm, $L/W = 50/294000$, S/D electrodes: Cr(10 nm)/Au(20 nm). [b] SiO_2: 200 nm, $L/W = 50/1000$, S/D electrodes: Au(50 nm). [c] SiO_2: 300 nm, $L/W = 50/500$, S/D electrodes: Cr(10 nm)/Au(20 nm).

grains of **2** and **3** are plate-like, similar to those of **1**, each grain is not lamellarly stacked, resulting in a rough surface. The grain sizes are larger and the surface is more smooth in **3** than in **2**.

The OFET devices were fabricated under several conditions and the characteristics of films deposited on HMDS-treated substrate at 50 °C are summarized in Table 1. Top contact devices generally showed higher performances than bottom contact ones because of better contacts between the electrodes and semiconductors in the former devices. In this case, however, the devices with bottom contact configuration had a tendency to show higher mobilities. This fact suggests that the anthraquinones have good contacts with electrodes, even in bottom contact devices. The top contact devices without HMDS treatment exhibited low mobilities (10^{-3}–10^{-5} $cm^2\ V^{-1}\ s^{-1}$ for **3**). Our bare-top contact devices had silanol groups at the SiO_2 surface since piranha clean was carried out. The acidic hydrogens of the silanol groups might have been coordinated to the carbonyl groups of the quinones, resulting in the formation of carrier traps. Therefore, passivation of the active surface would be important in the quinone systems.

The OFET devices based on **1** showed moderate mobilities, which were slightly lower than those of the corresponding anthracene derivative; however the threshold voltages were much lower.[8] It should be noted that anthraquinone **1** showed semiconducting behavior, although the effective conjugation length was short compared to usual semiconductors of OFETs. The FET characteristics were improved in films of **2** and **3** due to the increased conjugation length, as well as to the enhanced intermolecular interactions. The devices of **3** showed better performances (Fig. 4) than those of **2** and this result can be attributed to the difference in intermolecular interactions or film morphologies, as suggested in XRD and AFM measurements. The mobility of **3** was increased to 0.18 $cm^2\ V^{-1}\ s^{-1}$ (on : off ratio: 10^5, threshold voltage: 40 V) when a higher drain voltage ($V_D = 100$ V) was applied.

In summary, we have developed n-type FET devices based on novel anthraquinones for the first time as quinones. Although quinones have been considered to work in electron trapping, these findings have proved that quinones can afford high performance n-type FET devices. Since quinone units can be easily incorporated to π-conjugated systems, they would be useful as a core of n-type semiconductors for OFETs.

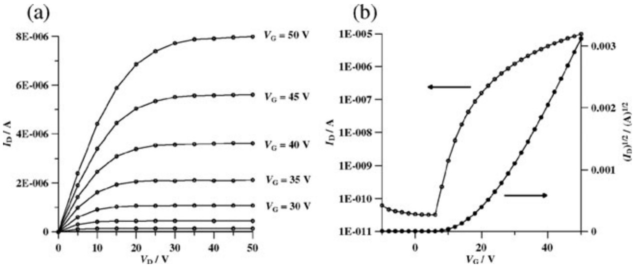


Fig. 4 (a) Output characteristics and (b) transfer characteristics of films of **3** deposited on HMDS-treated SiO_2 at 50 °C with top contact configuration.

This work was supported by a Grant-in-Aid for Scientific Research (no. 19350092) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, the Mizuho Foundation for the Promotion of Sciences, and the Global COE program "Education and Research Center for Emergence of New Molecular Chemistry". The author would like to thank Dr M. Yamasaki (Rigaku Co., Ltd.) for help with the X-ray structure analysis.

Notes and references

‡ The X-ray measurements of **1–3** were performed on a Rigaku R-AXIS RAPID imaging plate diffractometer with Mo-Kα radiation (λ = 0.71075 Å) at −180 °C. The structures were solved by the direct method (SIR97) and refined by the full-matrix least-squares method on F^2 with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were refined using the riding model and absorption correction was applied using an empirical procedure. **Crystal data for 1**: $C_{28}H_{14}F_6O_2$, M = 496.41, crystal dimensions 0.50 × 0.50 × 0.05 mm, monoclinic, space group $P2_1/n$, a = 8.1535(2), b = 8.1662(3), c = 31.2347(9) Å, β = 91.7150(9)°, V = 2078.77(11) Å^3, Z = 4, D_c = 1.586 g cm^{-3}, 19 754 reflections collected, 4761 independent (R_{int} = 0.026), GOF = 1.059, R_1 = 0.0394, wR_2 = 0.1104 for all reflections. CCDC reference number 709632. **Crystal data for 2**: $C_{36}H_{18}F_6O_2S_2$, M = 660.65, crystal dimensions 0.60 × 0.15 × 0.10 mm, triclinic, space group P-1, a = 7.7033(15), b = 10.4109(19), c = 17.980(3) Å, α = 73.309(4), β = 84.213(5), γ = 78.391(5)°, V = 1351.5(4) Å^3, Z = 2, D_c = 1.623 g cm^{-3}, 10 827 reflections collected, 4924 independent (R_{int} = 0.085), GOF = 0.964, R_1 = 0.0823, wR_2 = 0.2558 for all reflections. This R_1 is for the observed 2430 reflections. CCDC reference number 709633. **Crystal data for 3**: $C_{34}H_{16}F_6O_2N_2S_2$, M = 662.62, crystal dimensions 0.30 × 0.25 × 0.10 mm, triclinic, space group P-1, a = 12.2445(11), b = 13.2130(10), c = 14.4529(14) Å, α = 73.124(2), β = 73.488(2), γ = 65.1720(18)°, V = 1995.0(3) Å^3, Z = 3, D_c = 1.654 g cm^{-3}, 16 127 reflections collected, 7118 independent (R_{int} = 0.056), GOF = 0.955, R_1 = 0.0590, wR_2 = 0.1736 for all reflections. CCDC reference number 709634. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b820520e.

1 (*a*) M. Muccini, *Nat. Mater.*, 2006, **5**, 605; (*b*) L. Zhou, A. Wanga, S.-C. Wu, J. Sun, S. Park and T. N. Jackson, *Appl. Phys. Lett.*, 2006, **88**, 083502; (*c*) T. D. Anthopoulos, S. Setayesh, E. Smits, M. Cölle, E. Cantatore, B. de Boer, P. W. M. Blom and D. M. de Leeuw, *Adv. Mater.*, 2006, **18**, 1900; (*d*) T. Sekitani, M. Takamiya, Y. Noguchi, S. Nakano, Y. Kato, T. Sakurai and T. Someya, *Nat. Mater.*, 2007, **6**, 413; (*e*) D. R. Hines, V. W. Ballarotto and E. D. Williams, *J. Appl. Phys.*, 2007, **101**, 024503; (*f*) S. Ju, A. Facchetti, Y. Xuan, J. Liu, F. Ishikawa, P. Ye, C. Zhou, T. J. Marks and D. B. Janes, *Nat. Nanotechnol.*, 2007, **2**, 378.

2 (*a*) M. Halik, H. Klauk, U. Zschieschang, G. Schmid, S. Ponomarenko, S. Kirchmeyer and W. Weber, *Adv. Mater.*, 2003, **15**, 917; (*b*) M. M. Payne, S. R. Parkin, J. E. Anthony, C. C. Kuo and T. N. Jackson, *J. Am. Chem. Soc.*, 2005, **127**, 4986; (*c*) A. L. Briseno, S. C. B. Mannsfeld, M. M. Ling, S. Liu, R. J. Tseng, C. Reese, M. E. Roberts, Y. Yang, F. Wudl and Z. Bao, *Nature*, 2006, **444**, 913; (*d*) T. Yamamoto and K. Takimiya, *J. Am. Chem. Soc.*, 2007, **129**, 2224; (*e*) T. Izawa, E. Miyazaki and K. Takimiya, *Adv. Mater.*, 2008, **20**, 3388.

3 (*a*) A. Facchetti, *Mater. Today*, 2007, **10**, 28; (*b*) A. R. Murphy and J. M. J. Frechet, *Chem. Rev.*, 2007, **107**, 1066.

4 (*a*) R. J. Chesterfield, J. C. McKeen, C. R. Newman, P. C. Ewbank, D. A. da S. Filho, J. L. Bredas, L. L. Miller, K. R. Mann and C. D. J. Frisbie, *J. Phys. Chem. B*, 2004, **108**, 19281; (*b*) B. A. Jones, M. J. Ahrens, M.-H. Yoon, A. Facchetti, T. J. Marks and M. R. Wasielewski, *Angew. Chem., Int. Ed.*, 2004, **43**, 6363; (*c*) H. Z. Chen, M. M. Ling, X. Mo, M. M. Shi, M. Wang and Z. Bao, *Chem. Mater.*, 2007, **19**, 816; (*d*) R. Schmidt, M. M. Ling, J. H. Oh, M. Winkler, M. Konemann, Z. Bao and F. Wurthner, *Adv. Mater.*, 2007, **19**, 3692; (*e*) R. T. Weitz, K. Amsharov, U. Zschieschang, E. B. Villas, D. K. Goswami, M. Burghard, H. Dosch, M. Jansen, K. Kern and H. Klauk, *J. Am. Chem. Soc.*, 2008, **130**, 4637.

5 (*a*) M.-H. Yoon, S. A. DiBenedetto, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, 2005, **127**, 1348; (*b*) J. A. Letizia, A. Facchetti, C. L. Stern, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 2005, **127**, 13476; (*c*) T. Nakagawa, D. Kumaki, J. Nishita, S. Tokito and Y. Yamashita, *Chem. Mater.*, 2008, **20**, 2615; (*d*) H. Usta, A. Facchetti and T. J. Marks, *Org. Lett.*, 2008, **10**, 1385; (*e*) Y. Ie, Y. Umemoto, M. Okabe, T. Kusuniki, K. Nakayama, Y.-J. Pu, J. Kido, H. Tada and Y. Aso, *Org. Lett.*, 2008, **10**, 833.

6 Q. Miao, M. Lefenfeld, T.-Q. Nguyen, T. Siegrist, C. Kloc and C. Nuckolls, *Adv. Mater.*, 2005, **17**, 407.

7 (*a*) S. Ando, R. Murakami, J. Nishida, H. Tada, Y. Inoue, S. Tokito and Y. Yamashita, *J. Am. Chem. Soc.*, 2005, **127**, 14996; (*b*) K. Takimiya, Y. Kunugi, H. Ebata and T. Otsubo, *Chem. Lett.*, 2006, **35**, 1200; (*c*) T. Yasuda, M. Saito, H. Nakamura and T. Tsutsui, *Appl. Phys. Lett.*, 2006, **89**, 182108; (*d*) T. Kojima, J. Nishida, S. Tokito, H. Tada and Y. Yamashita, *Chem. Commun.*, 2007, **14**, 1430; (*e*) M. Mamada, J. Nishida, D. Kumaki, S. Tokito and Y. Yamashita, *Chem. Mater.*, 2007, **19**, 5404.

8 S. Ando, J. Nishida, E. Fujiwara, H. Tada, Y. Inoue, S. Tokito and Y. Yamashita, *Chem. Mater.*, 2005, **17**, 1261.