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[2,2′]Bi[naphtho[2,3-*b*]furanyl]: a versatile organic semiconductor with a furan–furan junction†

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[2,2′]Bi[naphtho[2,3-*b*]furanyl] was synthesized, characterized, and examined as an organic semiconductor for thin-film OFETs, bilayer OPVs, and organic light-emitting transistors (OLETs). In the devices, the material acted as a p-type semiconductor, showing moderately high mobility in OFETs, good photo conversion efficiency in OPVs, and blue-green emission in OLETs.

Extended π-conjugated molecules have recently been used as organic semiconductors applicable as active materials in organic electronic devices, such as organic light emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaics (OPVs).[1] Various aromatic and/or heteroaromatic cores have been utilized in the development of organic semiconductors. For example, linearly fused-benzene cores, so called oligoacenes, represent high performance organic semiconductors for OFET application,[2] and thiophene, a representative heteroaromatic core, has been widely utilized both for molecular and polymer semiconductors, well exemplified by poly(3-hexylthiophene).[3]

In these recent successful material developments, furan, another representative heteroaromatic, has been less studied compared to other heteroaromatics such as thiophene and pyrrole.[4] This could partially be attributed to chemical lability of furan and its derivatives; for example, furan serves as a diene in the [4 + 2] Diels–Alder reactions under milder conditions than those for thiophene and pyrrole.[5] On the other hand, relatively lower aromaticity of furan than thiophene and pyrrole may give rise to different electronic properties in the resulting furan-based materials.[6] In fact, we have recently reported a series of diphenyl-naphtho[2,3-*b*;5,6-*b*′]dichalcogenophenes (1–3, Fig. 1) and revealed that **1** is a fairly stable compound likely owing to the fused-furan structure, and furthermore, the lower aromaticity
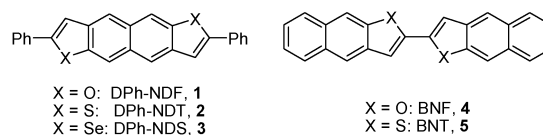
Fig. 1 Molecular structures of **1**–**5**.

of the fused-furan rings in **1** affords distinct molecular properties, *e.g.*, oxidation potential (or ionization potential, IP, at the thin film state) and absorption/emission properties, from those of the thiophene- (**2**) or selenophene counterparts (**3**).[7] More importantly, such differences in the molecular properties reflected their device characteristics; **1**-based bilayer solar cells fabricated with C_{60} afforded the best solar cell performances among the three, owing to their larger V_{oc} originating from **1**'s largest IP (*i.e.* deepest HOMO energy level) among the three.[7] These intriguing results prompted us to study fused-furan-containing extended π-systems. In this respect, we focus on a new furan-based compound, [2,2′]bi[naphtho[2,3-*b*]furanyl] (BNF, **4**) for the following reasons. First, as very limited compounds with furan–furan junction(s) have been examined as electronic materials so far, evaluations of **4** as an organic semiconductor can evaluate the potential of compounds with the furan–furan junction substructure. Second, smaller molecules consisting of less than four aromatic rings often show poor film forming properties, making it difficult to evaluate them as an organic semiconductor in the thin film devices, and thus **4** with six aromatic rings seems to be suitable for the evaluation of this class of compounds. Third, as its thiophene counterpart (**5**) has been already reported,[8] it is much easier to compare not only the molecular properties but also device characteristics in order to evaluate the effect of the different chalcogen atoms. Here, we report the synthesis, characterization, and device applications of **4**.

As the reported synthesis of naphtho[2,3-*b*]furan (NF) from 2-methoxynaphthalene is not very efficient,[9] we developed an improved synthesis from the same starting material by employing an *o*-selective functionalization of 2-methoxynaphthalene[10] and a facile furan formation reaction of 3-(2-trimethysilylethynyl)-2-acetoxynaphthalene (Scheme S1, ESI†).[11] Dimerization of NF easily afforded **4** in a moderate isolated yield after purification by vacuum sublimation. Structural determination was done by spectroscopic analyses as well as single crystal X-ray analysis (Fig. S1, ESI†). The molecule has an almost planar structure

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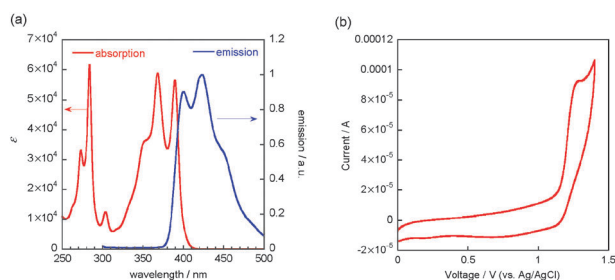
Fig. 2 Characterization of **4**: absorption (red trace) and emission (blue trace) spectra (a) and cyclic voltammogram (b).

Fig. 3 EQE spectra of **4**-based OPVs (a) and J–V characteristics under simulated AM 1.5 solar illumination (100 mW cm^{-2}) (b).

with dihedral angles close to 0°. The position of the oxygen atom in the five-membered ring is disordered as was reported for the thiophene counterpart (**5**).

Solution electrochemistry and absorption spectra of **4** revealed that the HOMO energy level (E_{HOMO}: ~-5.6 eV) and the HOMO–LUMO gap (E_g, 3.0 eV) of **4** are almost similar to those of **5** (Fig. 2, Table S1 and Fig. S2, ESI†).[8] On the other hand, emission properties of **4** and **5** are strikingly different; relatively weak emission was observed for **5** (ϕ_{PL} = 0.014), whereas **4** showed intensive emission with λ_{max} of 430 nm with fairly high quantum yield (ϕ_{PL} = 0.88).

OFET devices with a bottom-gate, top contact configuration were fabricated using the vapor deposited thin films of **4** on Si/SiO$_2$ substrates with surface modification with octyltrichlorosilane (OTS), octadecyltrichlorosilane (ODTS) or hexamethyldisilazane (HMDS) as a reagent. The **4**-based OFETs showed typical p-channel FET responses with the extracted mobility from the saturation regime of up to 0.21 cm^2 V^{-1} s^{-1} (Fig. S3, ESI†), which is almost comparable to those reported for the **5**-based transistors (0.67 cm^2 V^{-1} s^{-1}).[8] The surface morphology and crystallinity examined by AFM and XRD measurements indicate that the evaporated thin films of **4** are typical ones for vapor deposited molecular semiconductors, consisting of multi crystal grains with the edge-on molecular orientation (Fig. S4, ESI†).

We also tested **4** as the donor layer in the bilayer OPV with C$_{60}$ or C$_{70}$ as an acceptor layer with the device structure of ITO/**4** (40 nm)/C$_{60}$ or C$_{70}$ (30 nm)/BCP (10 nm)/Al (100 nm).[12] The absorption spectra of bilayer films (Fig. S5, ESI†) can be viewed as a superposition of both chromospheres; as **4** has relatively large E_g and therefore is almost transparent in the visible range, the acceptors seem to contribute as the major photosensitizer in the visible range. This consideration in fact agrees with external quantum efficiency (EQE) spectra, which is similar to the absorption spectra of C$_{60}$ thin films, and the relatively low short circuit current density (J_{sc}) of 2.22 mA cm^{-2} in the J–V characteristics of the **4**/C$_{60}$ OPV cells under simulated AM 1.5 solar illumination (100 mW cm^{-2}) is rationalized (Fig. 3). On the other hand, a fairly large open circuit voltage (V_{oc}) as high as 0.99 V was obtained, originating from the low-lying HOMO energy level of **4**. As a result, an overall power conversion efficiency (PCE) of 1.15% was achieved for the **4**/C$_{60}$ bilayer OPVs. Combination of **4** with C$_{70}$ possessing much enhanced absorption in the visible range[13] gave improved J_{sc} (3.66 mA cm^{-2}) with keeping a similar V_{oc} (1.04 V) and a fill factor (FF, 0.63), resulting in overall PCE of 2.39%. Although the PCEs were not very high compared to those of recently developed small-molecular and polymer-based
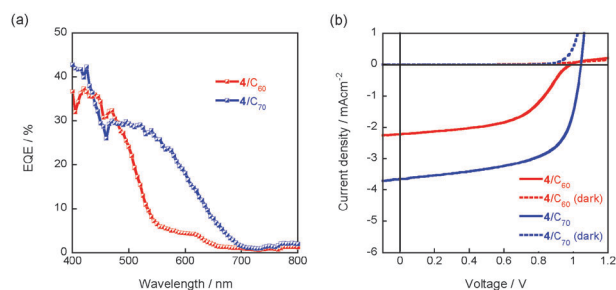
cells,[14] the higher V_{oc} (~1.0 V) regardless of the acceptor material is a characteristic feature of **4** as an electron donor from conventional electron donating materials often used in bilayer OPVs.[15]

One of the properties of **4** most different from those of **5** is the high PL efficiency in solution, and even in the solid state **4** showed fluorescence (Fig. S6, ESI†) with relatively high quantum efficiency (ϕ_{PL}; 0.72 for single crystals and 0.27 for evaporated thin films, respectively, see ESI†, Fig. S7). Taking the moderately high mobility in the thin film transistors into account, **4** can be regarded as a marked compound possessing good transport characteristics and highly efficient PL properties simultaneously in the solid state, implying that **4** is a potential material for light emitting transistor (LET) application, provided that both holes and electrons are injected.[16] Considering its high-lying LUMO energy level, we employed the top contact single crystal transistor configuration with asymmetric electrodes consisting of gold and calcium vacuum deposited through a shadow mask on vapor-grown single crystals (Fig. 4a, inset). Fig. 4 shows transfer characteristics of the transistors, where ambipolar transport was observed, thanks to the asymmetric electrodes. Extracted mobilities at the saturation regime were 0.1 cm^{-2} V^{-1} s^{-1} for holes and 0.04 cm^{-2} V^{-1} s^{-1} for electrons. As expected from the ambipolar FET characteristics,[16] the present transistor showed bright blue-green emission (Fig. 4b) with a maximum external quantum efficiency (EQE) of 0.27% at V_d = -100 V and V_g = -15 V. To the best of our knowledge, this is the first example of OLETs fabricated on a furan-based organic semiconductor. It should be also noted that the EQE of the present OLET is relatively high, compared to already reported OLETs with similar device structures using conventional organic semiconductors, such as tetracene, rubrene,[17] and p-distyrylbenzene (P3V2).[18] The present high performances could be explained by the fact that **4** has well-balanced high
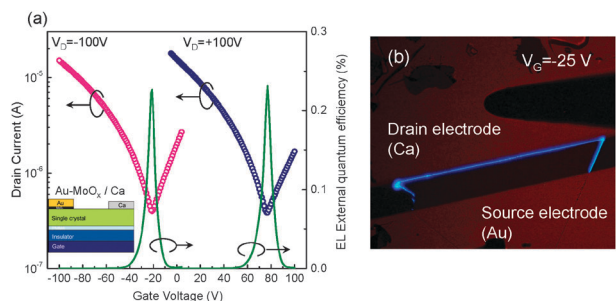

Fig. 4 Transfer characteristics of **4**-based OLETs (inset; device structure) (a) and photograph of an operating OLET device (b).

mobilities both for holes and electrons and high PL efficiency in the single crystal form.[19]

In conclusion, we demonstrated that **4** with a furan–furan junction is a versatile organic semiconductor with a p-type (hole-transporting) character for OFET, OPV, and OLET applications. Although furan-based organic semiconductors have been so far less studied in comparison to thiophene- or pyrrole-based ones, the present results indicate that furan-based materials may have a great potential as versatile organic semiconductors, in particular, their distinct photophysical properties in the solid state from those of the thiophene counterparts can make a new material class applicable to OPVs and OLETs. Developments of materials with fused-furan substructures are now ongoing in our research group.

Notes and references

1 *Organic Electronics, Manufacturing and Applications*, ed. H. Klauk, Wiley-VCH, Weinheim, 2006.
2 J. E. Anthony, *Angew. Chem., Int. Ed.*, 2008, **47**, 452.
3 (*a*) *Design and Synthesis of Conjugated Polymers*, ed. M. Leclerc and J.-F. Morin, Wiley-VCH, Weinheim, 2010; (*b*) I. Osaka and R. D. McCullough, *Acc. Chem. Res.*, 2008, **41**, 1202.
4 (*a*) H. Tsuji, C. Mitsui, L. Ilies, Y. Sato and E. Nakamura, *J. Am. Chem. Soc.*, 2007, **129**, 11902; (*b*) Y. Miyata, M. Terayama, T. Minari, T. Nishinaga, T. Nemoto, S. Isoda and K. Komatsu, *Chem.–Asian J.*, 2007, **2**, 1492; (*c*) J. C. Bijleveld, B. P. Karsten, S. G. J. Mathijssen, M. M. Wienk, D. M. de Leeuw and R. A. J. Janssen, *J. Mater. Chem.*, 2011, **21**, 1600; (*d*) Y. Li, P. Sonar, S. P. Singh, W. Zeng and M. S. Soh, *J. Mater. Chem.*, 2011,
21, 10829; (*e*) O. Gidron, Y. Diskin-Posner and M. Bendikov, *J. Am. Chem. Soc.*, 2010, **132**, 2148; (*f*) O. Gidron, A. Dadvand, Y. Sheynin, M. Bendikov and D. F. Perepichka, *Chem. Commun.*, 2011, **47**, 1976; (*g*) L. Huo, Y. Huang, B. Fan, X. Guo, Y. Jing, M. Zhang, Y. Li and J. Hou, *Chem. Commun.*, 2012, **48**, 3318; (*h*) C. Mitsui, J. Soeda, K. Miwa, H. Tsuji, J. Takeya and E. Nakamura, *J. Am. Chem. Soc.*, 2012, **134**, 5448.
5 M. Jones Jr., *Organic Chemistry*, 3rd edn, 2005.
6 A. Juric, A. Sabljic and N. Trinajstic, *J. Heterocycl. Chem.*, 1984, **21**, 273.
7 M. Nakano, H. Mori, S. Shinamura and K. Takimiya, *Chem. Mater.*, 2012, **24**, 190.
8 M. Mamada, J.-i. Nishida, D. Kumaki, S. Tokito and Y. Yamashita, *J. Mater. Chem.*, 2008, **18**, 3442.
9 N. S. Narasimhan and R. S. Mali, *Tetrahedron*, 1975, **31**, 1005.
10 (*a*) E. R. Biehl, A. R. Deshmukh and M. Dutt, *Synthesis*, 1993, 885; (*b*) K. Niimi, M. J. Kang, E. Miyazaki, I. Osaka and K. Takimiya, *Org. Lett.*, 2011, **13**, 3430.
11 (*a*) W.-M. Dai and K. W. Lai, *Tetrahedron Lett.*, 2002, **43**, 9377; (*b*) N. Hayashi, Y. Saito, H. Higuchi and K. Suzuki, *J. Phys. Chem. A*, 2009, **113**, 5342.
12 C. W. Tang, *Appl. Phys. Lett.*, 1986, **48**, 183.
13 J. Sakai, T. Taima, T. Yamanari and K. Saito, *Sol. Energy Mater. Sol. Cells*, 2009, **93**, 1149.
14 H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu and G. Li, *Nat. Photonics*, 2009, **3**, 649.
15 (*a*) K. L. Mutolo, E. I. Mayo, B. P. Rand, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.*, 2006, **128**, 8108; (*b*) Y. Kinoshita, T. Hasobe and H. Murata, *Appl. Phys. Lett.*, 2007, **91**, 083518; (*c*) M. D. Perez, C. Borek, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.*, 2009, **131**, 9281; (*d*) H. Mori and K. Takimiya, *Appl. Phys. Express*, 2011, **4**, 061602; (*e*) E. L. Brian, W. Guodan, W. Siyi, D. Z. Jeramy, V. D. Viacheslav, E. T. Mark and R. F. Stephen, *Appl. Phys. Lett.*, 2011, **98**, 243307.
16 F. Cicoira and C. Santato, *Adv. Funct. Mater.*, 2007, **17**, 3421.
17 T. Takenobu, S. Z. Bisri, T. Takahashi, M. Yahiro, C. Adachi and Y. Iwasa, *Phys. Rev. Lett.*, 2008, **100**, 066601.
18 H. Nakanotani, M. Saito, H. Nakamura and C. Adachi, *Appl. Phys. Lett.*, 2009, **95**, 033308.
19 S. Z. Bisri, T. Takenobu, Y. Yomogida, H. Shimotani, T. Yamao, S. Hotta and Y. Iwasa, *Adv. Funct. Mater.*, 2009, **19**, 1728–1735.