doi:10.1246/cl.2012.175

A Spin-carrying Naphthalenediimide Derivative with Azobenzene Unit

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(Received November 5, 2011; CL-111079; E-mail: nakatuji@sci.u-hyogo.ac.jp)

A naphthalenediimide derivative **3a** carrying TEMPO radical and azobenzene substituent was found to show photo-responsive magnetic as well as FET properties upon illumination. The alteration of its mobility has also been demonstrated by applying magnetic field and hence the FET characteristics of **3a** have been proven to be photo- as well as magneto-responsive.

There is a continuing trend in the field of molecular-based magnetic materials to develop multifunctional spin systems and considerable attention is paid to the development of organic functional radicals such as organic photochromic radicals,[1] organic thermochromic radicals,[2] liquid crystalline radicals,[3] organic conducting radicals,[4] or organic radical batteries.[5] During the course of our studies toward organic multifunctional spin systems based on nitroxide radicals,[6] we have been interested in developing organic functional radicals with photo-responsive properties and have to date reported some azobenzene derivatives carrying nitroxide radicals such as **1** (Chart 1).[7]

On the other hand, we also tried to develop organic functional radicals with FET properties and prepared recently several TEMPO-carrying naphthalenediimide (NDI) and perylenediimide (PDI) derivatives such as **2**[8] because of the beneficence of NDI and PDI units as the building blocks for n-channel OFET materials.[9] We then turned our attention to NDI derivatives carrying nitroxide radical together with *trans*-azobenzene-substituent (**3a**) to investigate their magnetic as well as FET properties and to see if changes of these properties would be possible upon irradiation or under magnetic field. We wish to report in this paper the structure and properties of the radical **3a**, which displays actual changes of magnetic as well as FET properties upon irradiation. Moreover, it was also verified that the FET characteristics could be tuned by applying magnetic field.

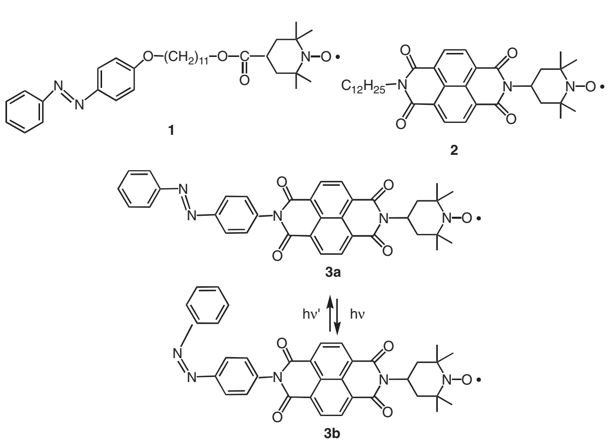

Chart 1.

The preparation of the radical compounds was performed in the usual manner starting from 1,4,5,8-naphthalenetetracarboxylic dianhydride, which was reacted with 4-amino-TEMPO and 4 aminoazobenzene in DMA with AcOH to give after separation of a couple of symmetrically substituted derivatives, the *trans*-azobenzene derivative **3a** in 23% yield. The first reduction potential (E_1^{RED}) of the compound should reflect its electron-accepting nature and is estimated by CV measurement (V vs. SCE, 0.1 M n-$\mathrm{BuN_4ClO_4}$ in dichloroethane at rt, scan rate: $50\,\mathrm{mV\,s^{-1}}$) to be −0.64 V, which is less negative that that of dodecyl derivative **2** (−0.78 V), indicating that **3a** is a stronger electron-acceptor than **2**.

As shown in Figure 1, the formation of π–π dimers is apparently seen in the crystal structure of **3a**[10] between couples of inner azobenzene units with the distances 3.967 and 3.797 Å, which in turn are contacted shortly by tilted layers of outer NDI units of other molecules with the distances of 3.437 and 3.458 Å, respectively. It is noteworthy that there exist relatively short contacts (3.190 and 3.094 Å) between the O atoms of TEMPO groups and the NDI units, suggesting existence of CT interactions between them.[11] Thus a unique supramolecular structure has been disclosed in the crystal structure of **3a**, although the lack of regular stacking of NDI units do not appear to be beneficial to the FET property.

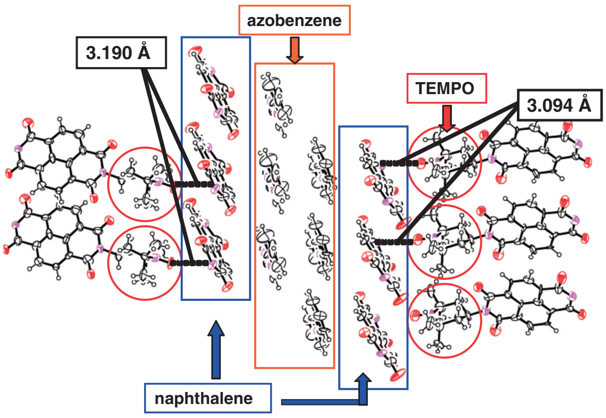

Figure 1. Crystal structure of **3a**, in which extracted structures with significant interactions are shown. The structure with eight molecules in a unit cell is shown in SI-1.[13]

Table 1. FET data of photoisomers[a]

Isomer	Mobility /$cm^2\,V^{-1}\,s^{-1}$	On/off ratio	Threshold /V
3a (original)	9.4×10^{-8}	2400	15.4
3b	5.7×10^{-8}	1300	9.6
3a (from 3b)	7.5×10^{-8}	2600	16.9

[a]Fabricated on Au bottom electrodes, SiO_2/Si substrates. SiO_2 surface was treated by HMDS.

The photochromic properties of this compound were demonstrated by irradiation with light of 365 nm. Thus the original absorption of 341, 360, and 380 nm gradually decreased by irradiation and in turn a broad absorption at around 435 nm gradually increased with isosbestic point at around 390 nm (SI-2[13]) and backward reaction was found to occur when the photoisomer **3b** was exposed to a fluorescent lamp (SI-3[13]). The isomer could be isolated as relatively stable solid substance when kept in the dark and stored in a refrigerator.

The magnetic properties of both photoisomers were found to show antiferromagnetic interactions of CW behavior but their Weiss temperatures are different (SI-4[13]). Namely, the magnitude of Weiss temperature of **3b** ($\theta = -1.13$ K) turns out to be almost half of that of **3a** ($\theta = -2.41$), indicating existence of weaker spin–spin interactions in the former isomer. The difference of their magnetic properties may reflect the difference of their crystal structures, although the crystal structure of the *cis*-isomer **3b** is not known yet.

It was of interest to see if the FET behavior could be tuned by the photoisomerization and then the thin layer of a device fabricated on Au bottom electrode with SiO_2/Si substrate treated by HMDS was irradiated repeatedly by a UV and vis lamp. The initial FET characteristics of *trans*-isomer are summarized in Table 1 and SI-5.[13] At first actual occurrence of photoisomerization was confirmed by the absorption change by irradiation at the thin film condition (SI-6[13]). At the same time, the change of FET properties of both photoisomers is observed along with the photoisomerization. Thus apparent changes of V_G-value of transfer data are observed from *trans* to *cis* and *cis* to *trans* by irradiation (Figure 2) and their values are summarized in Table 1. Although the mobilities are small for both isomers, each decrease of mobility, threshold voltage and on/off ratio was observed for *cis*-isomer together with the recovery of the original of *trans*-isomer by the next irradiation and thus the compound **3a** and **3b** was found to provide a unique example of azobenzene derivative displaying change of FET properties by *trans*–*cis* photoisomerization.

We then carried out an experiment to see the influence of applied magnetic field on the FET properties of **3a** (SI-7[13]). At first the measurements were performed for a device fabricated by using **3a** without applying magnetic field and its mobility ($3.45 \times 10^{-7}\,cm^2\,V^{-1}\,s^{-1}$) after annealing 150 °C, 15 min proved to be slightly higher than the data in Table 1 together with the lower on/off ratio (92) for this thin film device (SI-8[13]). However, apparent increase of its mobility almost twice as high as $6.24 \times 10^{-7}\,cm^2\,V^{-1}\,s^{-1}$ has been observed under applied magnetic field of 0.5 T (SI-9[13]) and this suggests occurrence of magnetic field effect on the mobility of a radical compound, even though the on/off ratio (91) has not been changed appreciably.[12] Although the exact reason for this effect on the mobility is not clear yet, it can be presumed from the experimental results that the electron mobility may be facilitated by applied magnetic field with some contribution of radical spin to result in its enhancement as the consequence. In addition, the magnetic field induced change in current remains surprisingly for at least 30 min after removing the magnetic field and it might be regarded as a kind of memory effect (SI-10[13]). Thus, a radical spin has been suggested to be workable as a sensing unit for physical properties such as FET under applied magnetic field.

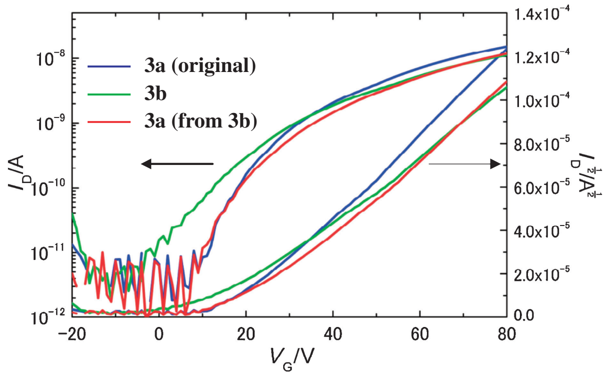

Figure 2. Change of FET data of **3a** by successive irradiation with UV and vis light.

In summary, azobenzene derivative **3a** has shown photochromism in solution as well as in thin film and the change of FET behavior has been revealed by the photoisomerization by illumination together with the change of magnetic properties. The alteration of mobility of **3a** has also been demonstrated by applying magnetic field to the thin film device and hence the FET characteristics of this compound have been proven to be photo- as well as magneto-responsive, thus providing a unique and unprecedented example of dual responsive system for FET properties.

We thank Prof. A. Kh. Vorobiev of Moscow State University for a preliminary UV–vis experiment on **3a**. This work was partially supported by a special grant of University of Hyogo and a grant for joint research project on nanoscience and device of ISIR, Osaka University, which are gratefully acknowledged.

References and Notes

1 a) S. Nakatsuji, *Chem. Soc. Rev.* **2004**, *33*, 348. b) K. Matsuda, M. Irie, *J. Photochem. Photobiol., C* **2004**, *5*, 169. c) G. I. Likhtenstein, K. Ishii, S. Nakatsuji, *Photochem. Photobiol.* **2007**, *83*, 871. d) J. Wang, L. Hou, W. R. Browne, B. L. Feringa, *J. Am. Chem. Soc.* **2011**, *133*, 8162.
2 a) W. Fujita, K. Awaga, *Science* **1999**, *286*, 261. b) W. Fujita, K. Awaga, H. Matsuzaki, H. Okamoto, *Phys. Rev. B* **2002**, *65*, 064434. c) Y. Morita, S. Suzuki, K. Fukui, S. Nakazawa, H. Kitagawa, H. Kishida, H. Okamoto, A. Naito, A. Sekine, Y. Ohashi, M. Shiro, K. Sasaki, D. Shiomi, K. Sato, T. Takui, K. Nakasuji, *Nat. Mater.* **2008**, *7*, 48. d) H. Nishimaki, T. Ishida, *J. Am. Chem. Soc.* **2010**, *132*, 9598. e) S. Matsumoto, T. Higashiyama, H. Akutsu, S. Nakatsuji, *Angew. Chem., Int. Ed.* **2011**, *50*, 10879.
3 a) R. Tamura, Y. Uchida, N. Ikuma, *J. Mater. Chem.* **2008**,

18, 2872. b) R. Tamura, *Nitroxides: Applications in Chemistry, Biomedicine, and Materials Science*, Wiley-VCH, Weinheim, **2008**, Chap. 9, p. 303. c) C. V. Yelamaggad, A. S. Achalkumar, D. S. S. Rao, M. Nobusawa, H. Akutsu, J.-i. Yamada, S. Nakatsuji, *J. Mater. Chem.* **2008**, *18*, 3433. d) S. Castellanos, F. López-Calahorra, E. Brillas, L. Juliá, D. Velasco, *Angew. Chem., Int. Ed.* **2009**, *48*, 6516. e) Y. Uchida, K. Suzuki, R. Tamura, N. Ikuma, S. Shimono, Y. Noda, J. Yamauchi, *J. Am. Chem. Soc.* **2010**, *132*, 9746.

4 a) T. Sugawara, M. M. Matsushita, *J. Mater. Chem.* **2009**, *19*, 1738. b) B. Rahman, H. Akutsu, J.-i. Yamada, K. Ohara, S. Nakatsuji, *Synth. Met.* **2009**, *159*, 1123. c) H. Komatsu, M. M. Matsushita, S. Yamamura, Y. Sugawara, K. Suzuki, T. Sugawara, *J. Am. Chem. Soc.* **2010**, *132*, 4528. d) H. Akutsu, S. Yamashita, J.-i. Yamada, S. Nakatsuji, Y. Hosokoshi, S. S. Turner, *Chem. Mater.* **2011**, *23*, 762.

5 a) K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro, E. Hasegawa, *Chem. Phys. Lett.* **2002**, *359*, 351. b) H. Nishide, T. Suga, *Electrochem. Soc. Interface* **2005**, *14*, No. 4, 32. c) L. Bugnon, C. J. H. Morton, P. Novak, J. Vetter, P. Nesvadba, *Chem. Mater.* **2007**, *19*, 2910. d) H. Nishide, K. Oyaizu, *Science* **2008**, *319*, 737. e) Y. Shibata, H. Akutsu, J.-i. Yamada, M. Satoh, U. S. Hiremath, C. V. Yelamaggad, S. Nakatsuji, *Chem. Lett.* **2010**, *39*, 671.

6 a) S. Nakatsuji, *Adv. Mater.* **2001**, *13*, 1719. b) S. Nakatsuji, *J. Synth. Org. Chem., Jpn.* **2003**, *61*, 670.

7 S. Nakatsuji, M. Fujino, S. Hasegawa, H. Akutsu, J.-i. Yamada, V. S. Gurman, A. Kh. Vorobiev, *J. Org. Chem.* **2007**, *72*, 2021.

8 S. Nakatsuji, K. Aoki, H. Akutsu, J.-i. Yamada, T. Kojima, J.-i. Nishida, Y. Yamashita, *Bull. Chem. Soc. Jpn.* **2010**, *83*, 1079.

9 F. Würthner, M. Stolte, *Chem. Commun.* **2011**, *47*, 5109, and references therein.

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

11 S. Nakatsuji, M. Nobusawa, H. Suzuki, H. Akutsu, J.-i. Yamada, *J. Org. Chem.* **2009**, *74*, 9345.

12 It has been clarified that the hydroxylamine derivative without radical spin obtained by the reduction of **3a** exhibits no intrinsic change of carrier mobility (from 1.8×10^{-7} to $2.1 \times 10^{-7}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) by applying a magnetic field (SI-11).

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