Annals of the Academy of Romanian Scientists
Series on Chemistry Sciences
Online ISSN 2393 – 2902 Volume 1, Number 1/2014

PHOTO-RESPONSIVE NAPHTHALENEDIIMIDE DERIVATIVE CARRYING A NITROXIDE AND AN AZOBENZENE GROUP

Miki NAKAGAWA[1], Hiroki AKUTSU[1], Jun-ichi YAMADA[1], Makoto KARAKAWA[2], Yoshio ASO[2], and Shin'ichi NAKATSUJI*[1]

Abstract. *A couple of naphthalenediimide derivatives carrying a nitroxide radical and an azobenzene group (4 and 5) were prepared as potentially photo-responsive radical compounds. While no clear photochromism could be discerned for 4 with p-amino-substituent, apparent photochromic property has been observed for 5 with p-dimethylamino-substituent by illumination in solution. N-type FET characteristics were observed for both of them even if their carrier mobilities were fairly small and the apparent changes of the characteristics were disclosed by photo-irradiation with UV light as well as successive heating for 5 at the thin film condition.*

Key words: *nitroxide, azobenzene, FET, photochromism, magnetic property*

Introduction

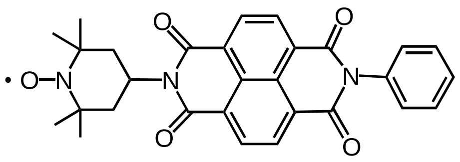
There is a growing interest in the search for effective organic semi-conducting materials for field effect transistors (OFET materials) because they are expected to be promising components in future electronics due to their possible applications such as integrated circuits for flexible electronics (Klauk H., 2006; Petty M. C., 2007; Wöll C., 2009). OFET materials with high-mobilities have so far been mainly p-type transistors and some of them show their device performances being comparable to those of amorphous silicon (Halik M. et al., 2003; Payne M. M. et al., 2005; Briseno A. L. et al., 2006; Yamamoto T. et al., 2007). On the other hand, the combination of p- and n-channel 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 undertook in the development of organic n-type FET materials (Chua L. L. et al., 2005; Facchetti A., 2007), e.g., fluorinated oligothiophenes, methallophathrocyanines, hetero-tetracyanoquinodimethanes, dicyanopyrazinoquinoxalines, or antharaquinones. Among them naphthalenediimide (NDI) derivatives (Katz H. E. et al., 2000; Kao C. C. et al., 2007) and perylenediimide (PDI) ones (Jones B. A. et al., 2004; Chen H. Z. et al.,

---

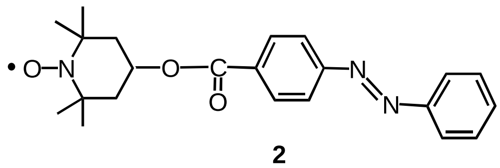
[*1] Graduate School of Material Science, University of Hyogo, 3-2-1 Kouto, Kamigori, Hyogo 678-1297, Japan, e-mail: nakatuji@sci.u-hyogo.ac.jp;
[2] Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan

2007; Weitz R. T. et al., 2008) have been regarded as attractive candidates for n-channel FETs.

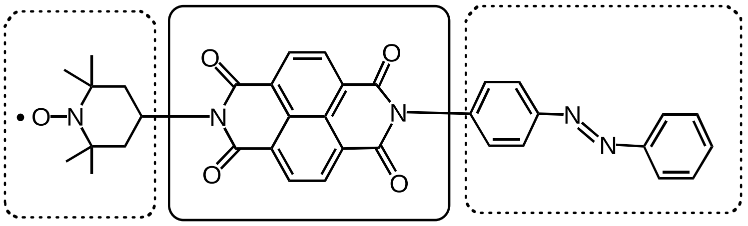
In the course of our studies toward organic magnetic materials with multi-functional properties (Nakatsuji S., 2004; Likhtenstein G. I. et al., 2007; Nakatsuji S., 2012), we have been interested in preparing organic spin systems with magnetic and possible FET properties and prepared several nitroxide-carrying NDIs and PDIs such as 1 (Chart) (Nakatsuji S. et al., 2010; Nakatsuji S. et al., 2013). We have also been interested in developing organic spin systems with photo-responsive property and reported so far on some azobenzene derivatives carrying a nitroxide radical such as 2 (Nakatsuji S. et al., 2007). Our next attention has been paid to NDI derivatives carrying a nitroxide radical together with an azobenzene group such as 3 to see if the changes of these properties would be possible upon irradiation and actually the NDI derivative 3 has been found to show photo-responsive magnetic as well as FET properties together with its magneto-responsive FET property (Nakagawa M. et al., 2012). We wish to report in this paper the preparation and properties of a couple of new NDI derivatives carrying a nitroxide radical and p-amino- or p-dimethylaminoazobenzene group (4 and 5) and the photo-responsive FET property of 5 by irradiation (Scheme 1).



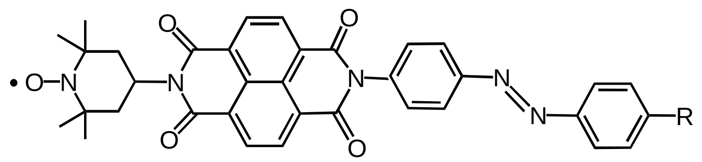
1



2



3

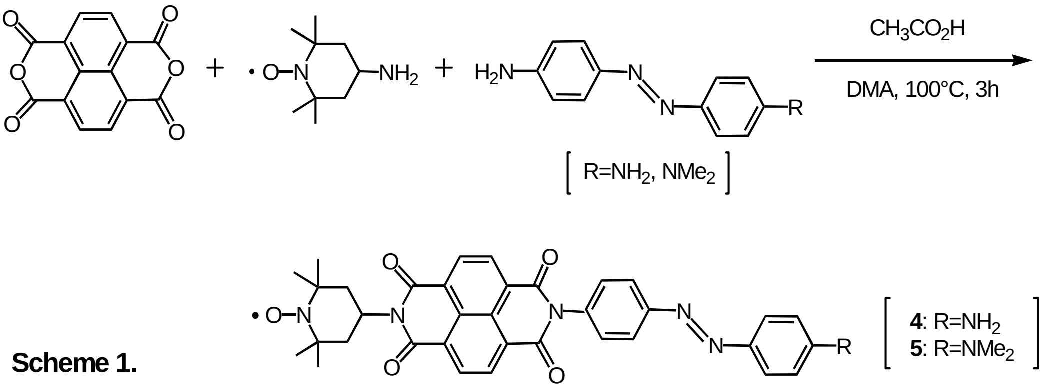


4: R=NH_2
5: R=NMe_2

Results and discussions

Preparation and redox properties of 4 and 5

The preparation of the NDI derivatives **4** and **5** was carried out as shown in Scheme 2 by using 1,4,5,8-naphthalenetetracarboxylic dianhydride as a starting material, which was reacted with 4-amino-TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) and 4,4'-diaminoazobenzene or 4-amino-4'-dimethylaminoazobenzene in DMA (dimethylacetamide) with small amount of AcOH to give after separation of a couple of symmetrically substituted derivatives, the NDI derivatives **4** in 7% and **5** in 26% yield respectively.



Scheme 1.

Their CV data of **4** and **5** are summarised in Table 1 together with those of **3**. The first oxidation potentials (E_1^{OX}) are corresponding to those of TEMPO units and the second ones (E_2^{OX}) are to amino groups respectively. Slightly weaker electron-donating properties are observed for **4** and **5** compared to **3** and it may due probably to the inductive effect of nitrogen atoms in **4** and **5**. The first and the second reduction potentials of **4** and **5** (E_1^{RED} and E_2^{RED}) are corresponding to those of NDI cores and oppositely stronger electron-accepting properties are found for **4** and **5** compared to **3**. The reason may also be understandable by considering the inductive effect of nitrogen atoms.

Table 1. CV data of NDI derivatives **4** and **5a** together with **3**[a]

Compound	E_2^{OX}	E_1^{OX}	E_1^{RED}	E_2^{RED}
4a	+ 1.05	+ 0.89	- 0.61	- 0.97
5a	+ 1.06	+ 0.89	- 0.59	- 1.07
3a[b]	-	+ 0.83	- 0.64	- 1.17

[a] V vs. SCE, 0.1 M n-Bu_4NClO_4 in DCE, scan rate 50 mV/s, rt. [b] Nakagawa M. et al., 2012.

Magnetic and FET properties of 4 and 5

The magnetic data of **4** and **5** were obtained by SQUID measurements between the temperature range of 2 K and 300 K and the data are summarized in Table 2 together with those of **3**.

Table 2. Magnetic data of NDI derivatives **4** and **5** together with **3**

Compound	Curie constant (emu K mol^{-1})	Weiss temperature (K)	Magnetic Interaction[a]
4	0.38	- 0.81	Antiferromagnetic
5	0.38	- 0.41	Antiferromagnetic
3[b]	0.38	- 2.41	Antiferromagnetic

[a] Fitting for Curie-Weiss law. [b] Nakagawa M. et al., 2012.

Their Curie constants reflect the existence of one spin per each molecule and weak antiferromagnetic interactions based on Curie-Weiss law are observed in all of them, being anticipated from their negative Weiss temperatures. Slightly stronger magnetic interactions are found in **4** than those in **5**, suggesting the presence of closer contact between the spin centers in **4** and still closer contact is presumed in **3** than in **4**.

The FET devices for the compounds **4** and **5** were fabricated with bottom-contact geometry on SiO_2/Si substrates by vapor-deposition. Gold electrodes forming channels of 5 mm length (*L*) and 38 mm width (W) were photolithographycally defined. The semiconductor layer (50 nm) was evaporated on the substrate surface, where the SiO_2 layer was 300 nm thick, and the derived data are summarized in Table 3 beneath.

Table 3. FET data of NDI derivatives **4** and **5**[a]

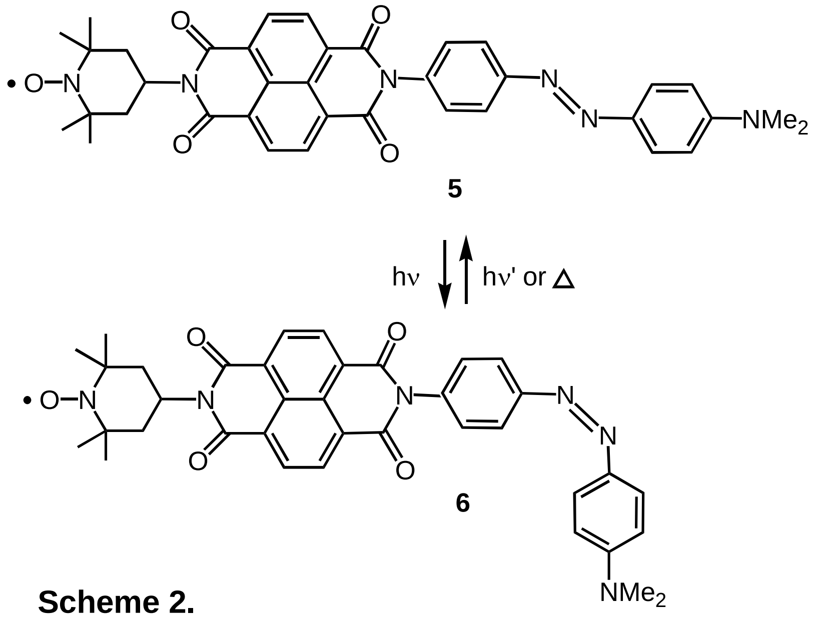
Compound	Mobility (cm^{2}V^{-1}s^{-1})	on/off ratio	Threshold (V)
4	3.4×10^{-9}	60	33.1
4 (after annealing)	1.0×10^{-8}	220	23.3
5	4.6×10^{-9}	57	29.3
5 (after annealing)	1.5×10^{-8}	168	20.6

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

Apparent exhibition of n-type FET properties was confirmed for both of them, even if their mobilities were rather small. As indicated in Table 2, the characteristics were found to be quite similar with each other and the enhancement of the characteristics was clarified by annealing at 150 °C for 15 min. for both of them, suggesting the tendency of adopting more appropriate molecular-orientations at the annealing condition.

Photochromic property of 5

The photocromic properties of the derivatives were investigated by irradiation with the light of 365 nm in dichloromethane solution. No distinct photo-isomerization could be found for **4** even by irradiation for a long period (1d~2d), although some slight change of the absorption spectra was perceived and then the corresponding cis-isomer could not be obtained actually. On the contrary, apparent change of its absorption spectra was observed for **5**. Thus the original absorptions at 360 and 380 nm as well as a broad absorption at around 440 nm decreased gradually by irradiation with UV lamp (365 nm) for 18 h (Fig. 1). In turn, the backward reaction was found to occur slowly when cis-isomer was exposed to a fluorescent lamp for several hours to reach a photo-stationary state in solution, namely, a broad absorption at around 550 nm increased with isosbestic point at around 490 nm but the complete change of the spectra could not be attained even after irradiation for 18h. The cis-isomer **6** could not be isolated as a solid substance presumably because of its unstable nature in the solid state.



Scheme 2.

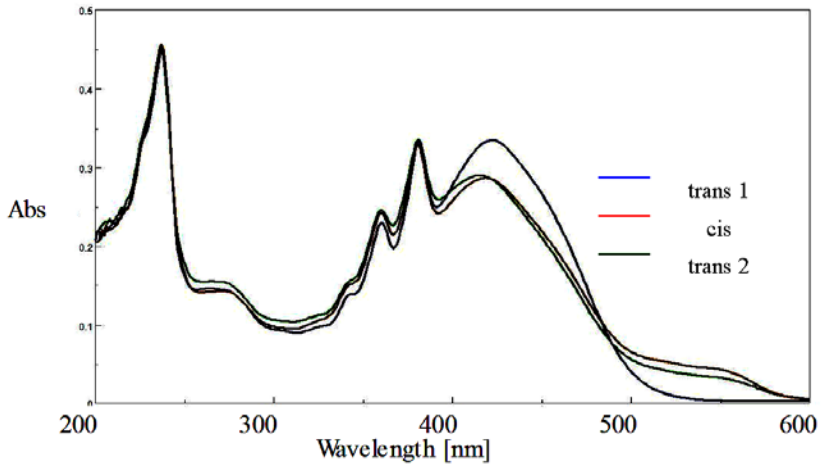


Fig. 1. Change of Absorption spectra of **5a** in dichloromethane solution by irradiation with UV and VIS light, where the blue line is the original spectra of **5a** (absorptions in arbitrary units). The red line indicates those after irradiation with UV light and green one after irradiation with a fluorescent lamp respectively.

It was of interest to see if the FET behavior could be tuned by the photo-isomerization and therefore the thin-layer device fabricated on Au bottom electrode with SiO_2/Si substrate treated by HMDS was irradiated and actual occurrence of photo-isomerization from the trans-isomer to the cis-isomer was confirmed by the similar absorption change with that in solution by irradiation with a UV lamp. In turn, the reverse reaction was found to proceed by merely heating at the thin film condition. At the same time, the change of FET properties of both photo-isomers is disclosed along with the isomerization. Thus apparent change of V_G-value is observed from trans to cis by irradiation with a UV lamp and cis to trans by heating as shown in Fig. 2 (transfer data) and their values are summarized in Table 4. Although the mobilities are small for both isomers, each decrease of mobility, on/off ratio as well as threshold voltage was observed for cis-isomer compared to initial values of trans-isomer. Moreover, the recovery of the values to those of original values was realized by heating and thus the compound **5** was found to provide a unique example of azobenzene derivative displaying changes of FET property by the isomerization.

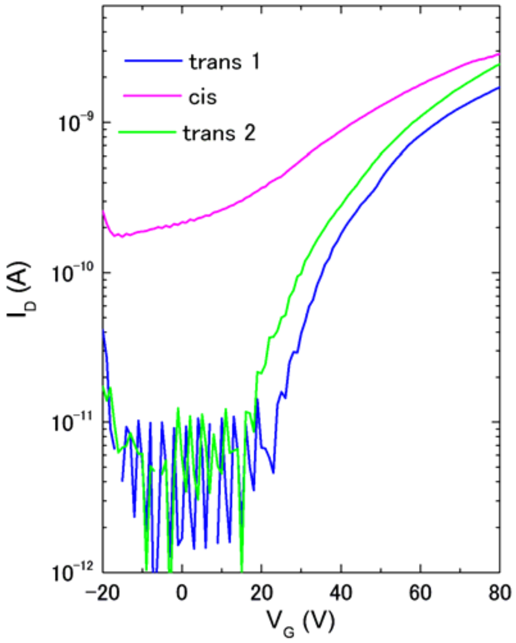


Fig. 2. Change of FET data of **5** by irradiation of UV light and successive heating.

Table 4 FET data of photo-isomers of **5**[a]

Isomer	Mobility ($cm^2V^{-1}s^{-1}$)	on/off ratio	Threshold (V)
Trans 1 (original)	$8.8x10^{-8}$	137	27.7
Cis	$9.5x10^{-9}$	10	- 10.7
Trans 2 (from Cis)	$1.5x10^{-8}$	168	20.6

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

Conclusions

A couple of NDI derivatives (**4** and **5**) carrying nitroxide and azobenzene groups have been prepared to investigate their magnetic and FET properties together with the possibility of occurrence of FET change upon irradiation. While no apparent occurrence of photochromic property could be discerned for **4** with p-aminoazobenzene group, actual occurrence of photochromsim and the significant FET change derived thereof have been disclosed for **5** with p-dimethylaminoazobenzene group, thus providing a unique example of spin system with photo-responsive FET property.

Experimental

Materials: The reagents used for the preparation of NDI derivatives described in the text were commercially available and were used without further purification.

Instrumentation: Melting points were measured on a Büchi M-565 apparatus and were uncorrected. MS spectra were taken using a JEOL JMS-AX 505 mass spectrometer and CV measurements were performed with BAS ALS/CHi612C electrochemical analyzer. 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.

Mobilities (μ) in FET data were calculated in the saturation regime by the relationship: $\mu_{\mathrm{sat}} = (2I_{\mathrm{D}}L)/[WC_{\mathrm{ox}}(V_{\mathrm{G}}\text{-}V_{\mathrm{th}})^2]$ where I_{D} is the source-drain saturation current: C_{ox} is the silicon oxide capacitance per unit area of the gate dielectric. 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} $(I_{\mathrm{D}})^{1/2}$ (Shukla D. et al., 2008)

Preparation of NDI derivatives: To a stirred solution of naphthalene-1,4,5,8-tetracarboxylic dianhydride (0.31 g, 1.17 mmol), 4,4'-diaminoazobenzene (0.24 g, 1.16 mmol), 4-amino-TEMPO (0.20 g, 1.20 mmol) in DMA (10 ml) was added acetic acid (1 ml) and the mixture was heated for 3 h at 100 °C. After cooling the reaction mixture, methanol (200 ml) was added and the precipitates were removed by filtration. The resulting filtrate was concentrated under reduced pressure and then purified by column chromatography (SiO_2; dichloromethane/diethyl ether) to give reddish solid. The recrystallization from dichloromethane yielded **4** as slightly hygroscopic reddish orange needles (40 mg, 7%). Mp. 270-273 °C; FAB-MS, m/z 617 (M+1); Anal. calcd for $C_{35}H_{31}N_6O_5{\bullet}0.5H_2O$: C, 67.30; H, 5.16; N, 13.45%. Found: C, 67.86; H, 5.57; N, 12.67%. In the similar manner, **5** was obtained as dark brown plates by using 4-dimethlamin-4'-aminoazobenzene in place of 4,4'-diaminoazobenzene in a better yield (26%). Mp. 263-265 °C; FAB-MS: 645 (M+1); Anal. calcd for $C_{37}H_{37}N_6O_5$: C, 69.04; H, 5.48; N, 13.06%. Found: C, 69.00; H, 5.53; N, 12.15%.

Acknowledgements

This work was partially supported by a special grant of University of Hyogo and a grant for joint research project on nano-science and device of ISIR, Osaka University, which are gratefully acknowledged.

References

Klauk H., (2006) - Organic Electronics: Materials, Manufacturing and Application, Wiley-VCH, Weinheim.

Petty M. C., (2007) - Molecular Electronics: From Principles to Practice, Wiley, Chichester.

Wöll C., (2009) - Physical and Chemical Aspects of Organic Electronics: From Fundamentals to Functional Devices, Wiley-VCH, Weinheim.

Halik M., Klauk H., Yschieschang U., Schmid G., Ponamarenko S., Kirchmezer S., Weber W., (2003) - Relationship Between Molecular Structure and Electrical Performance of Oligothiophene Organic Thin Film Transistors, Advanced Materials, 15 (11), 917-922.

Payne M. M., Parkin S. R., Anthony J. E., Kuo C. C., Jackson T. N., (2005) - Organic Field-Effect Transistors from Solution-Deposited Functionalized Acenes with Mobilities as High as 1 $cm^2/V \cdot s$, Journal of the American Chemical Society, 127 (14), 4986-4987.

Briseno A. L., Mannsfield S. C. B., Ling M. M., Liu S., Tseng R. J., C. Reese, Roberts M. E., Yang Y., Wudl F., Bao Z., (2006) - Patterning organic single-crystal transistor arrays, Nature, 444, 913-917.

Yamamoto T., Takimiya K., (2007) - Facile Synthesis of Highly π-Extended Heteroarenes, Dinaphtho[2,3-b:2‘,3‘-f]chalcogenopheno[3,2-b]chalcogenophenes, and Their Application to Field-Effect Transistors, Journal of the American Chemical Society, 129 (8), 2224-2225.

Chua L. L., Zaumseil J., Chang J. F., Ou E. C. W., Ho P. K. H., Sirringhaus H., Friend R. H., (2005) - General observation of n-type field-effect behaviour in organic semiconductors, Nature, 434, 194-199.

Facchetti A., (2007) - Semiconductors for organic transistors, Materials Today, 10 (3), 28-37.

Katz H. E., Lovinger A. J., Johnson J., Kloc C., Siegrist T., Li W., Lin Y. Y., Dodabalapur A., (2000) - A soluble and air-stable organic semiconductor with high electron mobility, Nature, 404, 478-481.

Katz H. E., Johnson J., Lovinger A. J., Li W., (2000) - Naphthalenetetracarboxylic Diimide-Based n-Channel Transistor Semiconductors: Structural Variation and Thiol-Enhanced Gold ContactsJournal of the American Chemical Society, 122 (32), 7787-7792.

Kao C. C., Lin P., Lee C. C., Wang Y. K., Ho J. C., Shen Y. Y., (2007) - High-performance bottom-contact devices based on an air-stable n-type organic semiconductor N,N-bis (4-trifluoromethoxybenzyl)-1,4,5,8-naphthalene-tetracarboxylic di-imide, Applied Physics Letters, 90 (21), 212101.

Jones B. A., Ahrens M. J., Yoon M. H., Facchetti A., Marks T. J., Wasielewski M. R., (2004) - High-Mobility Air-Stable n-Type Semiconductors with Processing Versatility: Dicyanoperylene-3,4:9,10-bis(dicarboximides), Angewante Chemie International Edition, 43 (46), 6363-6366.

Chen H. Z., Ling M. M., Mo X., Shi M. M., Wang M., Bao Z., (2007) - Air Stable n-Channel Organic Semiconductors for Thin Film Transistors Based on Fluorinated Derivatives of Perylene Diimides, Chemistry of Materials, 19 (4), 816-824.

Weitz R. T., Amsharov K., Zschieschang U., Villas E. B., Goswami D. K., Burghard M., Dosch H., Jansen M., Kern K., Klauk H., (2008) - Organic n-Channel Transistors Based on Core-Cyanated Perylene Carboxylic Diimide Derivatives, Journal of the American Chemical Society, 130 (14), 4637-4645.

Nakatsuji S., (2004) - Recent progress toward the exploitation of organic radical compounds with photo-responsive magnetic properties, Chemical Society Reviews, 33 (6), 348-353.

Likhtenstein G. I., Ishii K., Nakatsuji S., (2007) - Dual Chromophore-Nitroxides: Novel Molecular Probes, Photochemical and Photophysical Models and Magnetic Materials, Photochemistry and Photobiology, 83 (4), 871-881.

Nakatsuji S., (2012) - Recent progress in the chemistry of organic functional radicals, Environmental Engineering and Management Journal, 11 (11), 1889-1893.

Nakatsuji S., Aoki K., Akutsu H., Yamada J., Kojima T., Nishida J., Yamashita Y., (2010) - Spin-Carrying Naphthalenediimide and Perylenediimide Derivatives, Bulletin of the Chemical Society of Japan, 83 (9), 1079-1085.

Nakatsuji S., Aoki K., Kojoh A., Akutsu H., Yamada J., Karakawa M., Aso Y., (2013) - Self-Assembling Aryl-Naphthalendiimide Derivatives with a Nitroxide Radical, Asian Journal of Organic Chemistry, 2 (2), 164-168.

Nakatsuji S., Fujino M., Hasegawa S., Akutsu H., Yamada J., Gurman V. S., Vorobiev A. Kh., (2007) - Azobenzene Derivatives Carrying a Nitroxide Radical, The Journal of Organic Chemistry, 72 (6), 2021-2029.

Nakagawa M., Akutsu H., Yamada J., Karakawa M., Aso Y., Fall S., Heiser T., Nakatsuji, (2012) - A Spin-carrying Naphthalenediimide Derivative with Azobenzene Unit, Chemistry Letters, 41 (2), 175-177.

Shukla D., Nelson S. F., Freeman D. C., Rajeswaran M., Ahearn W. G., Meyer D. M., Carey J. T., (2008) - Thin-Film Morphology Control in Naphthalene-Diimide-Based Semiconductors: High Mobility n-Type Semiconductor for Organic Thin-Film Transistors, Chemistry of Materials, 20 (24), 7486-7491.