Paper in Celebration for the 2010 Nobel Prize in Chemistry

doi:10.1246/cl.2011.922

Synthesis and Properties of Seleno-analog MK-organic Dye for Photovoltaic Cells Prepared by C–H Functionalization Reactions of Selenophene Derivatives

Shunsuke Tamba,[1] Ryosuke Fujii,[1] Atsunori Mori,*[1] Kohjiro Hara,[2] and Nagatoshi Koumura*[2]
[1]*Department of Chemical Science and Engineering, Kobe University, Rokkodai, Nada, Kobe, Hyogo 657-8501*
[2]*Research Center for Photovoltaics, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565*

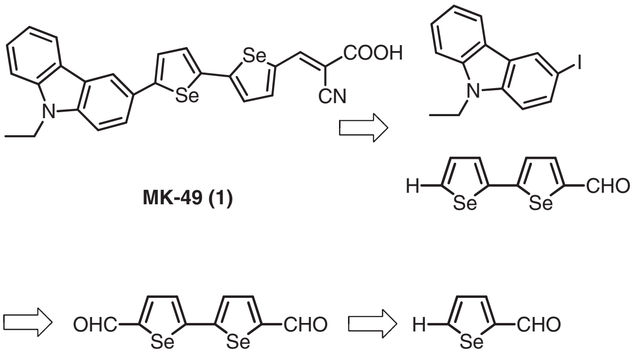
(Received April 6, 2011; CL-110287; E-mail: amori@kobe-u.ac.jp, n-koumura@aist.go.jp)

C–H arylation and homocoupling reactions of 2-formylselenophene were carried out with a palladium catalyst. By using these coupling reactions a seleno-analog of MK dye MK-49, which is an organic dye molecule of a dye-sensitized solar cell (DSSC), was synthesized. The performance of MK-49 as DSSC was compared with the corresponding thiophene dye MK-48.

Properties of heterocyclic organic molecules as advanced materials recently attract much attention particularly for sulfur-containing five-membered heteroaromatic compounds such as thiophenes and thiazoles.[1] Introduction of a substituent into the heterocyclic ring with transition-metal catalyst is a major concern in organic synthesis.[2] We have been engaged in the functionalization of such thiophenes at their carbon–hydrogen bonds by transition-metal catalysis and have shown that several C–H coupling reactions take place.[3]

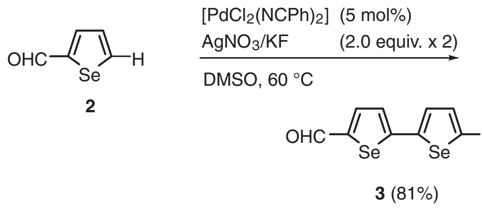
In contrast to a wide variety of cross-coupling reactions and C–H functionalization with sulfur-containing heteroaromatics, there are still few studies of the seleno-analog selenophenes.[4] It is thus intriguing to investigate the reactivity of the C–H bond of selenophene derivatives. Herein, we report C–H arylation and homocoupling reactions of selenophene derivatives with a palladium catalyst. In addition, synthesis and properties of a selenophene-analog of MK-dye[5] containing organic dye molecules for dye-sensitized photovoltaic cells,[6] are also described.

The dye molecule, which we envisaged to synthesize, is MK-49 (**1**) bearing a biselenophene unit, a carbazole dye moiety, and a cyanocarboxylate group. This compound would be synthesized by homocoupling of selenophene, mono-deformylation, C–H functionalization with halocarbazole and a following Knoevenagel condensation with cyanoacetic acid as summarized in Scheme 1.



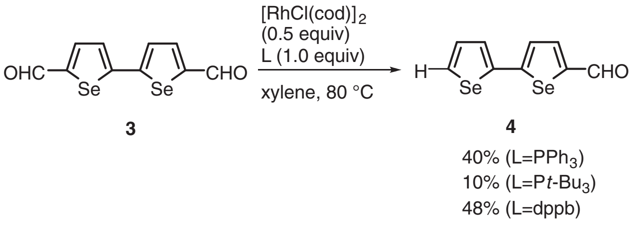
Scheme 1.

Homocoupling of 2-formylselenophene (**2**) in the presence of a palladium catalyst was first examined. We found that the optimal conditions for the homocoupling of 2-formylthiophene were available for the reaction of **2**.[3d] When the reaction was carried out with **2**, 5 mol % of [$PdCl_2(NCPh)_2$], and $AgNO_3$/KF (2.0 equiv × 2) in DMSO at 60 °C, 81% of the corresponding biselenophene **3** was obtained (Scheme 2).



Scheme 2.

Then, we performed mono-deformylation of diformylbiselenophene **3** in the presence of a rhodium complex [RhCl(cod)]$_2$ in xylene at 80 °C as shown in Scheme 3. Several phosphane ligands were added to rhodium. Among these, the use of bidentate dppb exhibited superior performance to afford the corresponding formylbiselenophene **4** in 48% yield while other phosphanes resulted in lower yields.[7,8]

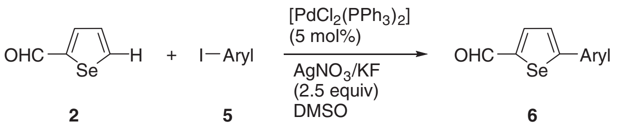


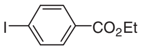
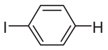
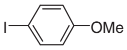
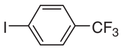
Scheme 3.

We next studied the C–H arylation reaction with formylselenophene **2** toward several aryl iodides. As shown in Table 1, the reactivity of selenophene was found slightly inferior to the corresponding thiophene.[3b] The reaction of ethyl 4-iodobenzoate (**5a**) under similar conditions for the reaction of 2-formylthiophene to proceed smoothly in high yield resulted in giving the corresponding coupling product **6** in 27% yield. The use of increased amount of $AgNO_3$/KF (2.50 equiv) at elevated temperature (100 °C) improved the yield to 69%. Other aryl iodides such as iodobenzene, 4-iodoanisole, and 4-iodobenzotrifluoride also underwent C–H arylation in 46 to 50% yields.

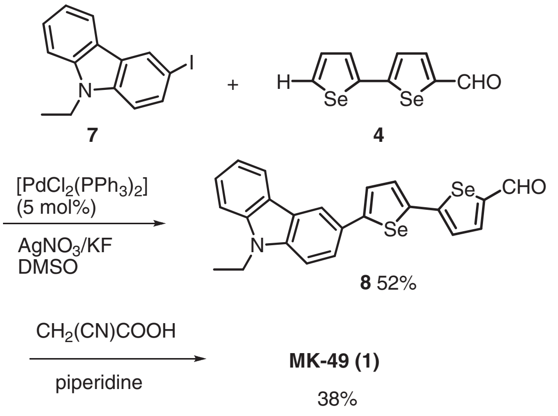
The C–H arylation reaction was employed for the reaction of formylbiselenophene **4** with 9-ethyl-3-iodocarbazole (**7**) in the presence of $AgNO_3$/KF (Scheme 4). The corresponding coupling product **8** was afforded in 52% yield. Then, the formylbiselenophene was transformed into cyanocarboxylate

Table 1. C–H arylation of 2-formylselenophene (**2**)[a]



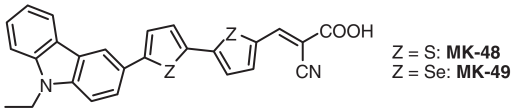
I-Aryl		AgNO$_3$/KF /equiv	Temp /°C	Yield[b] /%
	(**5a**)	1.25	60	27
		2.5	100	69
	(**5b**)	2.5	100	50
	(**5c**)	2.5	100	46
	(**5d**)	2.5	100	48

[a] The reaction was carried out with 0.6 mmol of **2** and 0.5 mmol of **4** in 2 mL of DMSO for 5 h. [b] Isolated yield.



Scheme 4.

Table 2. UV–vis absorption and photoluminescent spectra of dyes MK-48 and MK-49



Dye	Solution[a]		Film
	$\lambda_{\rm abs}$/nm ($\varepsilon \times 10^{-4}$/M^{-1} cm^{-1})	$\lambda_{\rm em}{}^{\rm b}$/nm	$\lambda_{\rm abs}$/nm
MK-48	471 (3.49)	566	414
MK-49	490 (3.34)	589	429

[a] Absorption and emission data were obtained in 20%THF–toluene solution. [b] Excited at 480 nm.

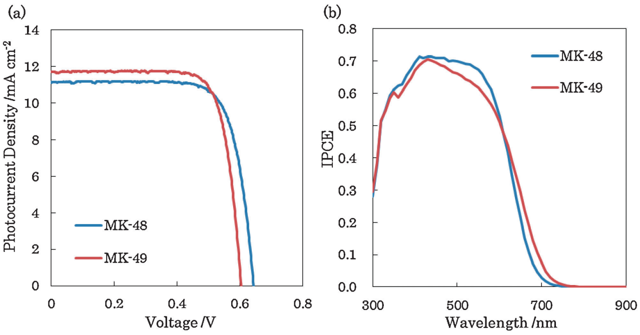


Figure 1. Photovoltaic performance for MK-48 and MK-49: (a) current density–voltage characteristics and (b) IPCE spectra.

Table 3. DSSCs performance parameters of the dyes[a]

Dye	$J_{\rm sc}$/mA cm^{-2}	$V_{\rm oc}$/V	FF	η/%
MK-48	11.24	0.636	0.757	5.41
MK-49	11.92	0.599	0.763	5.44

[a] For details: See refs. 5b and 11.

(MK-49) with cyanoacetic acid in the presence of piperidine (38% yield).

Studies on the properties of the obtained MK-49 as a dye-sensitized photovoltaic cell were carried out comparing with the corresponding thiophene analog MK-48. Table 2 summarizes the results.[9] Measurements of UV–vis absorption and photoluminescent spectra indicated that absorption and emission maxima of MK-49 were approximately 20 nm higher than those of the thiophene analog MK-48, whereas MK-48 and -49 showed similar ε values. However, these values were found to be much higher than that of ruthenium-based N3 dye (ca. 16000 M^{-1} cm^{-1}).[10] When these dyes were adsorbed onto transparent TiO$_2$ films, there were significant blue shifts of the absorption peaks (ca. 60 nm). This is probably due to specific interaction between the dyes or deprotonation of the dye on TiO$_2$.

Figure 1a shows the photocurrent density–voltage characteristics for dye-sensitized solar cell (DSSC) of MK-48, and MK-49. The short-circuit photocurrent density ($J_{\rm sc}$) was found to be ca. 11–12 mA cm^{-2} and the open-circuit photovoltage ($V_{\rm oc}$) was ca. 0.6 V in both MK-48 and MK-49.

As shown in Figure 1b,[11] broadening of the incident photo-to-current conversion efficiency (IPCE) spectra to longer wavelength toward that of MK-48 was shown in MK-49, however the lower maximum IPCE of the DSSC in MK-49 was observed in the range of 400–600 nm region.

Table 3 summarizes the DSSC performance of MK-48 and -49. Under standard global AM 1.5G irradiation (100 mW cm^{-2}), the MK-49-sensitized solar cell gave superior performance in $J_{\rm sc}$ (ca. 0.7 mA cm^{-2}), whereas the $V_{\rm oc}$ value of MK-49 was found to be slightly lower than that of MK-48 (0.04 V). The product of J and V values at the maximum power point was also similar thus leading to little difference in fill factor (FF) values. By these complimentary results, power conversion efficiency η (%) values were mostly equal in MK-48 and -49 dyes, accordingly.

In summary, homocoupling and C–H arylation reactions of selenophene were revealed to take place similarly to thiophene. With the C–H functionalization protocols a short synthesis of MK-49, which is a class of organic dye used in photovoltaic cells, was performed and physical properties of MK-49 and the corresponding thiophene analog MK-48 were compared.[9]

This work was partially supported by a Grant-in-Aid for Scientific Research (B) by Japan Science Promotion Society. The authors thank Nara Institute of Science and Technology, Kyoto-Advanced Nanotechnology Network, supported by Ministry of Education, Culture, Sports, Science and Technology, Japan for measurements of high-resolution mass spectra.

This paper is in celebration of the 2010 Nobel Prize awarded to Professors Richard F. Heck, Akira Suzuki, and Ei-ichi Negishi.

References and Notes

1 a) J. M. Tour, *Chem. Rev.* **1996**, *96*, 537. b) S. Günes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev.* **2007**, *107*, 1324. c) Y.-J. Cheng, S.-H. Yang, C.-S. Hsu, *Chem. Rev.* **2009**, *109*, 5868. d) H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, D. M. de Leeuw, *Nature* **1999**, *401*, 685. e) D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* **2000**, *100*, 2537. f) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.* **2009**, *109*, 897. g) I. Osaka, R. D. McCullough, *Acc. Chem. Res.* **2008**, *41*, 1202.

2 For reviews: a) L.-C. Campeau, K. Fagnou, *Chem. Commun.* **2006**, 1253. b) O. Daugulis, V. G. Zaitsev, D. Shabashov, Q.-N. Pham, A. Lazareva, *Synlett* **2006**, 3382. c) T. Satoh, M. Miura, *Chem. Lett.* **2007**, *36*, 200. d) I. V. Seregin, V. Gevorgyan, *Chem. Soc. Rev.* **2007**, *36*, 1173. e) L.-C. Campeau, D. R. Stuart, K. Fagnou, *Aldrichimica Acta* **2007**, *40*, 35. f) C. A. Zificsak, D. J. Hlasta, *Tetrahedron* **2004**, *60*, 8991. g) F. Kakiuchi, T. Kochi, *Synthesis* **2008**, 3013. h) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174. i) A. Mori, A. Sugie, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 548.

3 a) A. Mori, A. Sekiguchi, K. Masui, T. Shimada, M. Horie, K. Osakada, M. Kawamoto, T. Ikeda, *J. Am. Chem. Soc.* **2003**, *125*, 1700. b) K. Kobayashi, A. Sugie, M. Takahashi, K. Masui, A. Mori, *Org. Lett.* **2005**, *7*, 5083. c) M. Takahashi, K. Masui, H. Sekiguchi, N. Kobayashi, A. Mori, M. Funahashi, N. Tamaoki, *J. Am. Chem. Soc.* **2006**, *128*, 10930. d) K. Masui, H. Ikegami, A. Mori, *J. Am. Chem. Soc.* **2004**, *126*, 5074. e) N. Masuda, S. Tanba, A. Sugie, D. Monguchi, N. Koumura, K. Hara, A. Mori, *Org. Lett.* **2009**, *11*, 2297. f) S. Tamba, Y. Okubo, S. Tanaka, D. Monguchi, A. Mori, *J. Org. Chem.* **2010**, *75*, 6998. g) S. Matsuda, M. Takahashi, D. Monguchi, A. Mori, *Synlett* **2009**, 1941.

4 a) K. Karabelas, A. Hallberg, *J. Org. Chem.* **1986**, *51*, 5286. b) P. Prediger, A. V. Moro, C. W. Nogueira, L. Savegnago, P. H. Menezes, J. B. T. Rocha, G. Zeni, *J. Org. Chem.* **2006**, *71*, 3786. c) O. S. do Rêgo Barros, A. Favero, C. W. Nogueira, P. H. Menezes, G. Zeni, *Tetrahedron Lett.* **2006**, *47*, 2179. d) Đ. T. Tùng, A. Villinger, P. Langer, *Adv. Synth. Catal.* **2008**, *350*, 2109.

5 a) N. Koumura, Z.-S. Wang, S. Mori, M. Miyashita, E. Suzuki, K. Hara, *J. Am. Chem. Soc.* **2006**, *128*, 14256. b) Z.-S. Wang, N. Koumura, Y. Cui, M. Takahashi, H. Sekiguchi, A. Mori, T. Kubo, A. Furube, K. Hara, *Chem. Mater.* **2008**, *20*, 3993. c) M. Miyashita, K. Sunahara, T. Nishikawa, Y. Uemura, N. Koumura, K. Hara, A. Mori, T. Abe, E. Suzuki, S. Mori, *J. Am. Chem. Soc.* **2008**, *130*, 17874. d) N. Koumura, Z.-S. Wang, M. Miyashita, Y. Uemura, H. Sekiguchi, Y. Cui, A. Mori, S. Mori, K. Hara, *J. Mater. Chem.* **2009**, *19*, 4829. e) X.-H. Zhang, Z.-S. Wang, Y. Cui, N. Koumura, A. Furube, K. Hara, *J. Phys. Chem. C* **2009**, *113*, 13409. f) S. Tanba, A. Sugie, N. Masuda, D. Monguchi, N. Koumura, K. Hara, A. Mori, *Heterocycles* **2010**, *82*, 505. g) X.-H. Zhang, Y. Cui, R. Katoh, N. Koumura, K. Hara, *J. Phys. Chem. C* **2010**, *114*, 18283.

6 a) M. Grätzel, *Inorg. Chem.* **2005**, *44*, 6841. b) A. Hagfeldt, M. Grätzel, *Chem. Rev.* **1995**, *95*, 49. c) B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737. d) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* **2010**, *110*, 6595. e) R. Li, X. Lv, D. Shi, D. Zhou, Y. Cheng, G. Zhang, P. Wang, *J. Phys. Chem. C* **2009**, *113*, 7469.

7 a) J. Tsuji, K. Ohno, *Tetrahedron Lett.* **1965**, *6*, 3969. b) M. C. Baird, J. T. Mague, J. A. Osborn, G. Wilkinson, *J. Chem. Soc. A* **1967**, 1347. c) J. Blum, E. Oppenheimer, E. D. Bergmann, *J. Am. Chem. Soc.* **1967**, *89*, 2338.

8 Formylbiselenophene **4** has been prepared with Stille coupling. H. Nakanishi, S. Inoue, T. Otsubo, *Mol. Cryst. Liq. Cryst.* **1997**, *296*, 335.

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

10 M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.* **1993**, *115*, 6382.

11 DSC conditions: irradiated light: AM 1.5 (100 mW cm^{-2}); photoelectrode: TiO_2 (14 µm thickness and 0.2399 cm^2 area); electrolyte: 0.60 M 1,2-dimethyl-3-propylimidazolium iodide (DMPImI)/0.05 M iodine (I_2)/0.10 M lithium iodide (LiI)/0.50 M 4-*tert*-butylpyridine (TBP) in acetonitrile.