

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

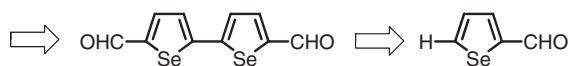
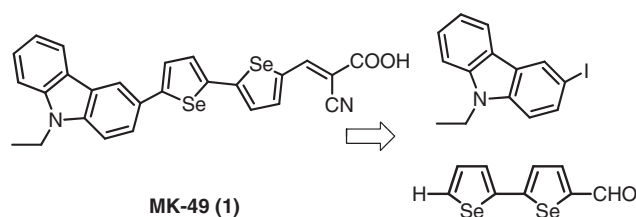
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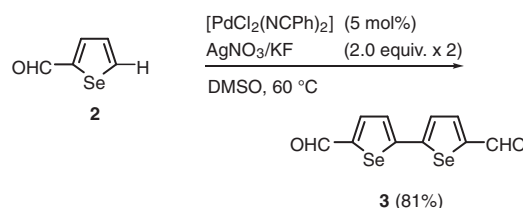
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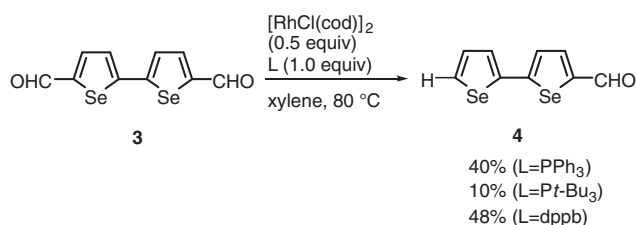
C–H arylation and homocoupling reactions of 2-formylselenophene were carried out with a palladium catalyst. By using these coupling reactions a seleno-analog of MK dye MK-49, which is an organic dye molecule of a dye-sensitized solar cell (DSSC), was synthesized. The performance of MK-49 as DSSC was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



Scheme 1.



Scheme 2.



Scheme 3.

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-dye⁵ 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.

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 [PdCl₂(NCPH)₂], and AgNO₃/KF (2.0 equiv × 2) in DMSO at 60 °C, 81% of the corresponding biselenophene **3** was obtained (Scheme 2).

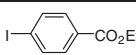
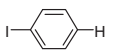
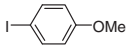
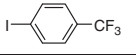
Then, we performed mono-deformylation of diformylbiselenophene **3** in the presence of a rhodium complex [RhCl(cod)]₂ in xylene at 80 °C as shown in Scheme 3. Several phosphane ligands were added to rhodium. Among these, the use of bidentate dppb exhibited superior performance to afford the corresponding formylbiselenophene **4** in 48% yield while other phosphanes resulted in lower yields.^{7,8}

We next studied the C–H arylation reaction with formylselenophene **2** toward several aryl iodides. As shown in Table 1,

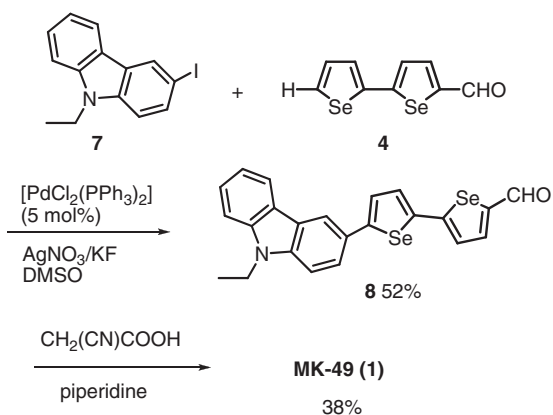
the reactivity of selenophene was found slightly inferior to the corresponding thiophene.^{3b} The reaction of ethyl 4-iodobenzoate (**5a**) under similar conditions for the reaction of 2-formylthiophene to proceed smoothly in high yield resulted in giving the corresponding coupling product **6** in 27% yield. The use of increased amount of AgNO₃/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 AgNO₃/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

$\text{OHC}-\text{C}_4\text{H}_3\text{Se}-\text{H} + \text{I}-\text{Aryl} \xrightarrow[\text{DMSO}]{\text{[PdCl}_2(\text{PPh}_3)_2] \text{ (5 mol\%)} \text{ AgNO}_3/\text{KF} \text{ (2.5 equiv)}} \text{OHC}-\text{C}_4\text{H}_2\text{Se}-\text{Aryl}$			
2	5	6	
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

^aThe reaction was carried out with 0.6 mmol of **2** and 0.5 mmol of **4** in 2 mL of DMSO for 5 h. ^bIsolated yield.

**Scheme 4.**

(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 TiO₂ 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 TiO₂.

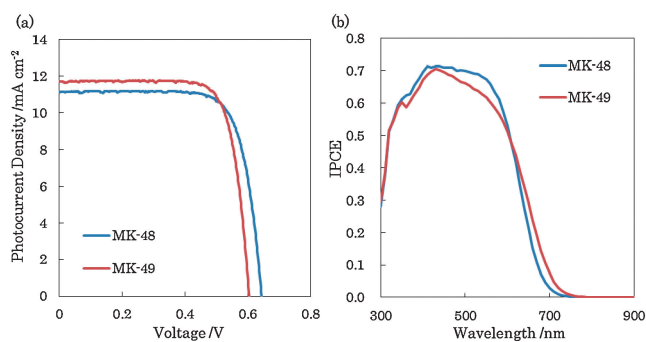
Figure 1a shows the photocurrent density–voltage characteristics for dye-sensitized solar cell (DSSC) of MK-48, and MK-49. The short-circuit photocurrent density (J_{sc}) was found to be ca. 11–12 mA cm⁻² and the open-circuit photovoltage (V_{oc}) was ca. 0.6 V in both MK-48 and MK-49.

As shown in Figure 1b,¹¹ broadening of the incident photo-to-current conversion efficiency (IPCE) spectra to longer wave-

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

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

^aAbsorption and emission data were obtained in 20% THF–toluene solution. ^bExcited 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	$J_{sc}/\text{mA cm}^{-2}$	V_{oc}/V	FF	$\eta/\%$
MK-48	11.24	0.636	0.757	5.41
MK-49	11.92	0.599	0.763	5.44

^aFor details: See refs. 5b and 11.

length 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_{sc} (ca. 0.7 mA cm⁻²), whereas the V_{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.

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