
Shunsuke Tamba,1 Ryosuke Fujii,1 Atsunori Mori,1 Kohjiro Hara,2 and Nagatoshi Koumura*2

1Department of Chemical Science and Engineering, Kobe University, Rokkodai, Nada, Kobe, Hyogo 657-8501
2Research 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-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 biseselenophene 3 was obtained (Scheme 2).

Then, we performed mono-deformylation of diformylbiselenophene 3 in the presence of a rhodium complex [RhCl(cod)]2 as a solvent in Scheme 3. Several phosphine ligands were added to rhodium. Among these, the use of bidentate dpdb exhibited superior performance to afford the corresponding formylbiseselenophene 4 in 48% yield while other phosphines 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 (2.5 equiv) at elevated temperature (100 °C) improved the yield to 69%. Other aryl iodides such as idobenzenes, 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 formylbiseselenophene 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 formylbiseselenophene was transformed into cyanocarboxylate.
Table 1. C–H arylation of 2-formylselenophene (2)

<table>
<thead>
<tr>
<th>I-Aryl</th>
<th>AgNO₃/KF (5 mol%)</th>
<th>Temp /°C</th>
<th>Yield /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂Et</td>
<td>1.25</td>
<td>60</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>100</td>
<td>69</td>
</tr>
<tr>
<td>H</td>
<td>2.5</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>OMe</td>
<td>2.5</td>
<td>100</td>
<td>46</td>
</tr>
<tr>
<td>CF₃</td>
<td>2.5</td>
<td>100</td>
<td>48</td>
</tr>
</tbody>
</table>

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. Isolated yield.

**(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. 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). 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 and 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 (Jₘₚ) was found to be ca. 11–12 mA cm⁻² and the open-circuit photovoltage (Vₖ) was ca. 0.6 V in both MK-48 and MK-49.

As shown in Figure 1b, broadening of the incident phototo-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 Jₘₚ (ca. 0.7 mA cm⁻²), whereas the Vₖ 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.

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


11 DSC conditions: irradiated light: AM 1.5 (100 mW cm⁻²); photoelectrode: TiO₂ (14 μm thickness and 0.2399 cm² area); electrolyte: 0.60 M 1,2-dimethyl-3-propylimidazolium iodide (DMPImI)/0.05 M iodine (I₂)/0.10 M lithium iodide (LiI)/0.50 M 4-tert-butyldipyridine (TBP) in acetonitrile.