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Regio- and stereo-selective intermolecular [2+2] cycloaddition of allenol esters with C_{60} leading to alkylidenecyclobutane-annulated fullerenes†

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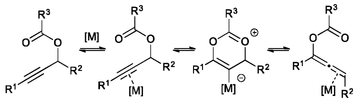
The intermolecular [2+2] cycloaddition of allenol esters, which were *in situ* generated by Pt-catalyzed 1,3-acyloxy migration of propargylic esters, with C_{60} proceeded regio- and stereo-selectively to give a novel class of alkylidenecyclobutane-annulated fullerenes. The cyclobutane-annulated fullerene derivatives have high-lying LUMO levels, which gave a high open-circuit voltage in organic solar cell applications. The observed high electron mobility provided a good fill factor compared with the PCBM-based devices.

Ring annulated fullerenes have attracted considerable attention because PCBM ([6,6]-phenyl-C_{61}-butyric acid methyl ester), which is a cyclopropane-annulated fullerene, displays outstanding performance as a material for organic photovoltaics (OPVs).[1] In this research field, we are particularly interested in functionalized cyclobutane-annulated fullerenes. Despite the tremendous efforts devoted to the synthesis of cyclobutane annulated fullerenes based on [2+2] cycloaddition reactions,[2,3] application studies as a material for OPVs were still insufficient to discover a cyclobutane-annulated fullerene that exhibits a high performance as a material. This is in sharp contrast to the fact that studies on cyclopropane- or cyclopentane-annulated fullerenes have been pursued vigorously.[4]

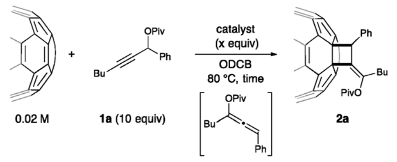
In this study, encouraged by the recent progress in the *in situ* generation of allenol esters from propargylic esters by transition-metal catalysts (Scheme 1),[5–9] we envisaged the [2+2] cycloaddition of *in situ* generated allenol esters with C_{60}, which would give a novel class of alkylidenecyclobutane-annulated fullerenes.



Scheme 1 Transition-metal catalyzed 1,3-acyloxy migration of propargylic esters.

In the first investigation, when a mixture of propargylic ester **1a** and C_{60} was treated with 0.5 equiv. of $AuCl(PPh)_3$ in 1,2-dichlorobenzene (ODCB) at 80 °C for 6 h, no reaction took place (Table 1, entry 1).[10] However, when we used $PtCl_2$ as a catalyst for 1,3-acyloxy migration of **1a** under similar conditions, the [2+2] cycloaddition product **2a** was obtained in 21% yield as a single isomer (Table 1, entry 2). Prolonging the reaction time to 18 h resulted in a significant improvement in the yield of **2a** to 47% (Table 1, entry 3). The amount of $PtCl_2$ was reduced to 0.1 equiv. without a decrease in the yield (Table 1, entries 4 and 5). In entry 4, the isolated yield of **2a** was 31%, whereas the yield based on the amount of C_{60} consumed was 67%. In the case of entries 2–5, multiple cycloaddition products were also

Table 1 Intermolecular [2+2] cycloaddition of *in situ* generated allenol esters (from **1a**) with C_{60}[a]



Entry	Catalyst	*x* equiv.	Time (h)	Yield of **2a**[b] (%)
1	$AuCl(PPh_3)$	0.5	6	0
2	$PtCl_2$	0.5	6	21
3	$PtCl_2$	0.5	18	47
4	$PtCl_2$	0.1	18	45 (31, 67)
5	$PtCl_2$	0.05	18	37

[a] Reaction conditions: C_{60} (0.15 mmol), **1a** (10 equiv.), transition-metal (*x* equiv.) in ODCB (7.5 mL) at 80 °C. [b] Determined by the HPLC area ratio. The values in parentheses are the isolated yield of **2a** (left) and the yield of **2a** on the basis of the amount of C_{60} consumed (right).

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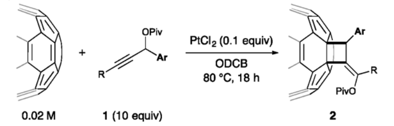
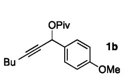
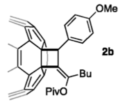
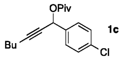
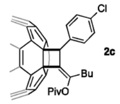
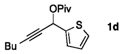
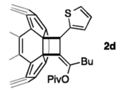
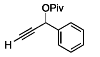
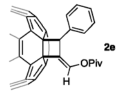
Table 2 Intermolecular [2+2] cycloaddition of *in situ* generated allenol esters (from **1**) with C_{60}[a]



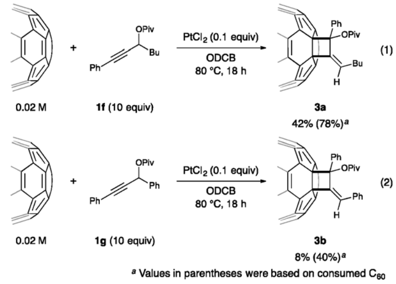
Entry	**1**	Yield of $\mathbf{2}^b$ (%)
1		 40 (88)
2		 31 (69)
3		 35 (57)
4		 33 (68)

[a] Reaction conditions: C_{60} (0.15 mmol), **1** (10 equiv.), $PtCl_2$ (0.1 equiv.) in ODCB (7.5 mL) at 80 °C for 18 h. [b] Isolated yield of **2**. The values in parentheses are based on the amount of C_{60} consumed.

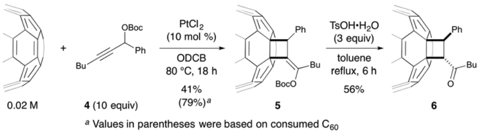
detected as side products by LC-MS analysis. The structure of **2a** was characterized using HRMS and NMR techniques (^{1}H, ^{13}C, DEPT, HMQC, HMBC, and NOESY) after purification using silica-gel column chromatography (see the ESI†). The geometry of the product **2a** was the *Z*-isomer, which was presumably because of the steric repulsion between the Bu group and C_{60}.

Having adopted the optimized conditions mentioned in entry 4, we next explored the scope of the intermolecular [2+2] cycloaddition of **1** with C_{60}. The reaction of **1b** with C_{60} gave the corresponding [2+2] cycloaddition product **2b** in 40% yield (Table 2, entry 1). The propargylic ester **1c** bearing a *p*-chlorophenyl group also reacted with C_{60} to afford **2c** in 31% yield (entry 2). The propargylic ester **1d** bearing a 2-thienyl group displayed higher reactivity than **1a**, and in this case, a large amount of multiple cycloaddition products was also formed (entry 3). The terminal acetylene **1e** tolerated the reaction conditions to furnish the corresponding [2+2] cycloaddition product **2e** in 33% yield. The geometry of the product **2e** was *E*-isomer due to the steric repulsion of the OPiv group towards the fullerene ring (entry 4).

We also examined the propargylic ester **1f** having a phenyl acetylene moiety (Scheme 2-1). Surprisingly, in this case, the fullerene **3a**, which was derived *via* [2+2] cycloaddition with the pivaloxyalkene portion, was obtained in 42% yield regio- and stereo-selectively. The 1,3-diphenyl-substituted propargylic ester **1g** also afforded the similar cyclobutanol-annulated fullerene **3b**, albeit in low yield. In this case, the conversion of C_{60} was low (HPLC analysis: **3b**/multiple cycloaddition products/C_{60} = 12/13/70) and a [2+2] dimerization product of the *in situ* generated allenol ester was observed (Scheme 2-2).[8]



Scheme 2 Intermolecular [2+2] cycloaddition of *in situ* generated allenol ester (from **1f** and **1g**) with C_{60}.



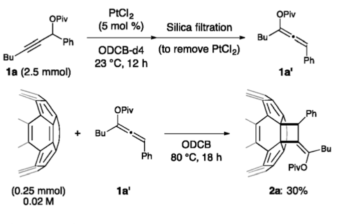
Scheme 3 Reaction of C_{60} with carbonate **4** to give **5** and **6**.

Using a similar protocol, the propargylic carbonate **4** was successfully reacted with C_{60} to give the corresponding adduct **5** in 41% yield, which was further converted into the ketone **6** by acidic treatment with $TsOH{\cdot}H_2O$ (Scheme 3).

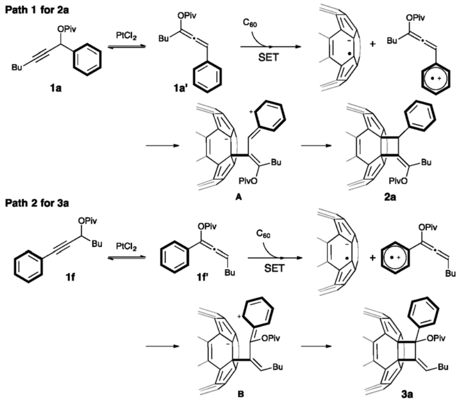
To confirm the stepwise reaction *via* the formation of an allenol ester, we carried out the reaction of C_{60} with the isolated allenol ester **1a′**, which was obtained by the Pt-catalyzed 1,3-acyloxy migration of **1a** and purified by silica filtration to remove $PtCl_2$. As we expected, the product **2a** was obtained in 30% yield (Scheme 4).

A plausible mechanism for the present cycloaddition is illustrated in Scheme 5. The activation of the propargylic ester **1a** by the platinum catalyst would induce a 1,3-acyloxy migration to generate the allenol ester **1a′**. A single-electron transfer (SET) from the aryl group of allenol ester **1a′** to C_{60} would then occur to give a radical ion pair[11,12,13,14] consisting of the radical anion $C_{60}^{\bullet-}$ and a radical cation of **1a′**. The radical anion $C_{60}^{\bullet-}$ would react regioselectively with the radical cation of **1a′** to give the [2+2] cycloaddition product **2a** *via* the zwitterionic intermediate **A** (Scheme 5, path 1 for **2a**). In the case of **1f**, which gave a regioisomer, a similar zwitterionic intermediate **B** would be formed *via* a SET pathway from the aryl group of the allenol ester **1f′** to C_{60} to give **3a** (path 2 for **3a**). We deem that in both cases SET with the benzene ring is crucial for the regioselective reaction.

To determine the physical properties of the alkylidenecyclobutane-annulated fullerenes prepared in this study, we chose **2a**



Scheme 4 Control experiments.



Scheme 5 Plausible mechanism.

and the hydrolyzed ketone **6** as model probes. Optical bandgaps were derived from the UV-visible absorption spectra of **2a** and **6** (see Fig. S1 and S2 in the ESI†), which were 1.71 eV for both compounds. The electrochemical properties were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) (see Fig. S3 and S4 in the ESI†). The lowest unoccupied molecular orbital (LUMO) levels were estimated from the DPV data. The LUMO levels of **2a** and **6** (−3.71 and −3.69 eV, respectively) were higher than those of $PC_{61}BM$ (−3.74 eV for PCBM, determined by CV in dichloromethane).[15] These results promise to provide a high open-circuit voltage (V_{OC}) in organic solar cell applications.

We investigated the photovoltaic performance of the obtained fullerene derivatives as electron acceptors in standard bulk heterojunction organic solar cells using P3HT as an electron donor (Table 3, Fig. 1). Solubilities of these electron acceptors in organic aromatic solvents were respectable, which were similar to PCBM, enabling thin-film fabrication with active layer solvents at similar concentrations for the standard P3HT:PCBM bulk heterojunction devices. First of all, we examined donor : acceptor ratios in the photoactive layer from 5 : 3 to 2 : 3. The best donor : acceptor ratio for devices using **2a** was 1 : 1, whereas that for devices employing **6** was 5 : 4. Notably, these ratios are almost the same as the ratio in a P3HT : PCBM device. The devices were thermally annealed at 120 °C. The obtained V_{OC} of devices using **2a** (0.60 ± 0.004 V) was slightly higher than that of a device using PCBM (0.58 V) because of the high-lying LUMO levels of this fullerene derivative. The power conversion efficiencies (PCEs) of P3HT:**2a** and P3HT:**6** were 0.95 ± 0.015% and 2.64 ± 0.020%, respectively. The low PCE of the device using **2** is attributable to the large volume of the Piv group, which hampers fullerene–fullerene interactions.[16] With **6** exhibiting the best performance, we tried to increase the PCE of the P3HT:**6** device by modifying the solution concentration of the active layer and the annealing temperature after spin-coating. The PCE reached 2.96 ± 0.05% (the best performance was 3.00%) with a good fill factor (FF, 0.65) and short-circuit current density (J_{SC}, 8.60 mA cm^{-2}) when the concentration was 30 mg mL^{-1}, and the annealing temperature was 150 °C. We fabricated devices employing these conditions with other fullerene derivatives, but the PCE decreased because their solubility was lower than that of **6**. Finally, we used the low band-gap polymer PTB7 as an electron donor instead of P3HT and obtained a PCE of 3.78% with a V_{OC} of 0.74 V, J_{SC} of 8.28 mA cm^{-2}, and FF of 0.62 without using additives (Table 3). The PCE was higher than that of a device using $PC_{61}BM$[17] (PCE = 3.6%, V_{OC} = 0.71 V, J_{SC} = 9.5 mA cm^{-2}, and FF = 0.53) with a good V_{OC} and FF.

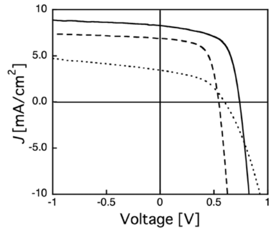


Fig. 1 *J–V* characteristics of the P3HT:fullerene derivatives and PTB7:**6** organic solar cells; dotted line, P3HT:**2a**, dashed line, P3HT:**6**, and solid line, PTB7:**6**.

Table 3 Summary of the device performances of the bulk heterojunction organic solar cells

Acceptor	Donor	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [−]	PCE[a] [%]
2a	P3HT[b]	0.60 (0.595 ± 0.005)	3.45	0.47	0.97 (0.95)
6	P3HT[b]	0.53 (0.534 ± 0.003)	8.60	0.65	3.00 (2.96)
6	PTB7[c]	0.74 (0.737 ± 0.004)	8.28	0.62	3.78 (3.73)

[a] The average values are in the parentheses. [b] Poly(3-hexylthiophene-2,5-diyl). [c] Poly(4,8-bis[(2-ethylhexyl)benzo[1,2-*b*:4,5-*b*′]dithiophene-2,6-diyl]{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-*b*]thiophenediyl}).

We hypothesized that the relatively high FFs compared with those of PCBM devices were derived from the high electron mobility of **6** or good film morphology. The electron mobility of the electron-only devices was measured using a space-charge-limited current (SCLC) method (see Fig. S5 and S6 in the ESI†). The device structures were Al/active layer/LiF (0.6 nm)/Al. The electron mobilities of the P3HT:**6** and PTB7:**6** devices were 1.3×10^{-4} and 4.1×10^{-4} cm^2 V^{-1} s^{-1} with the active-layer film thickness of 310 and 150 nm, respectively. These electron mobilities were higher than those obtained from P3HT:PCBM and PTB7:PCBM electron-only devices.[18] The morphologies of the P3HT:**6** devices were investigated by atomic force microscopy (see Fig. S7 in the ESI†). In agreement with the performance obtained for the devices annealed at 120 and 150 °C, high temperature annealing increased the surface roughness, which probably led to a good FF and mobility. On the other hand, the PTB7:**6** film had a smoother surface compared with the P3HT:**6** film. This implies the high miscibility of PTB7 and **6**. We ascribe this to the high solubility of **6**.

In conclusion, we have developed the regio- and stereo-selective intermolecular [2+2] cycloaddition of *in situ* generated allenol esters with C_{60}. For the regioselective cycloaddition of allenol esters with C_{60}, we proposed pathways involving a radical ion-pair formed by a SET process. Measuring the physical properties of **2a** and ketone **6** for comparison with PCBM, we obtained a respectable PCE of 3.78% using PTB7 with ketone **6** with a good V_{OC} (0.74 V) and FF (0.62), which were derived from the high-lying

LUMO level and higher electron mobility of ketone **6**, respectively (V_{OC} and FF of a $PC_{61}BM$ device are 0.71 V and 0.53, respectively).

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Notes and references

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11 In the case of using undec-6-yn-5-yl pivalate as an aliphatic substrate, despite the corresponding allenol ester was observed, the desired product was not obtained and all C_{60} was recovered. This result exhibits that the nucleophilic attack of allenol esters to C_{60} does not seem to be involved in the reaction mechanism because the aliphatic allenol ester generally shows the same nucleophilicity as the aromatic allenol ester (see ref. 7).

12 In the chemistry of fullerenes, many reactions of C_{60} *via* single-electron transfer (SET) process are known. See: ref. 4.

13 It is well known that C_{60} acts as an effective electron transfer (ET) inhibitor (see ref. 4*b*). Therefore, to the best of our knowledge, there are no examples that ET scavenger has acted as the inhibiter effectively in the reaction of C_{60} *via* SET. Actually, although we used an excess amount of 1,4-dinitrobenzen as an ET scavenger under the conditions of Table 2, the yield of the reaction of **1b** with C_{60} did not decrease.

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