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# Synthesis of 1,4-diaryl[60]fullerenes by bis-hydroarylation of C<sub>60</sub> and their use in solution-processable, thin-film organic photovoltaic cells

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# ABSTRACT

An AlCl<sub>3</sub>-mediated Friedel–Crafts reaction of arenes with  $C_{60}$  affords two-fold hydroarylated compounds,  $C_{60}Ar_2H_2$ , which upon deprotonation with <sup>t</sup>BuOK and oxidation with CuBr·SMe<sub>2</sub> yield 1,4-diaryl[60]fullerenes,  $C_{60}Ar_2$  (Ar = Ph, 4-Me-C<sub>6</sub>H<sub>4</sub>, 3,4-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>, and 4-Ph-C<sub>6</sub>H<sub>4</sub>) in good yield. A solution-processed, thinfilm organic photovoltaic device using  $C_{60}$ (4-PhC<sub>6</sub>H<sub>4</sub>)<sub>2</sub> as electron acceptor material showed a 2.3% power conversion efficiency..

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There is enormous interest in thin-film organic photovoltaic (OPV) devices,  $^{1,2}$  in which fullerene derivatives<sup>3</sup> serve as a key *n*type semiconductor component. Most of the reported studies use a single compound, PCBM (phenyl C61-butyric acid methyl ester),<sup>4</sup> which is a cyclopropane, that is, two C-C bonds next to each other, and hence referred to as a 1,2-diadduct, or its congeners. We have recently reported the synthesis of 1,4-dialkyl[60]fullerene derivatives, SIMEFs (bis(silylmethyl)[60]fullerenes),<sup>5</sup> and their application as electron-acceptor materials for OPV devices.<sup>2</sup> This 1,4adduct has a higher LUMO level than those of the 1,2-diadducts such as PCBMs and gives a higher open-circuit voltage ( $V_{OC}$ ). Although a few examples of the synthesis of 1,4-diaryl[60]fullerenes have already been reported,<sup>6</sup> methods for the synthesis of 1,4-diadducts have been less explored than for their 1,2-counterparts.<sup>7</sup> Herein, we report the synthesis of 1,4-diaryl[60]fullerene derivatives (2a-d) in two steps-an AlCl3-mediated Friedel-Crafts hydroarylation reaction<sup>8</sup> followed by dehydrogenation (Table 1). This two-step approach is unique among other routes to 1,4-diorganofullerenes for its use of a diorganodihydro compound (1a-d) as an intermediate, and it alleviates the use of expensive reagents-an attractive character for a large-scale synthesis of fullerene derivatives. The substituents on the aryl groups allow us to tune the solubility and the physical properties of the molecules, and a solution-processed, thin-film organic photovoltaic device using **2d** showed 2.3% power conversion efficiency.

Through modification of the conditions that we previously developed for the synthesis of triaryltrihydro[60]fullerenes,<sup>8</sup> we first synthesized diaryldihydro[60]fullerenes,  $C_{60}Ar_2H_2$  (**1a–d**), after which the product was dehydrogenated by sequential treatment with <sup>t</sup>BuOK and CuBr·SMe<sub>2</sub> to obtain the desired diaryl[60]fullerenes **2a–d** (Table 1).<sup>9</sup> The reaction time and the stoichiometry, in particular, that of water (1 equiv to fullerene),

Table 1

Synthesis of 1,4-diaryl[60]fullerenes by  ${\sf AlCl}_3\text{-mediated}$  bis-hydroarylation of  ${\sf C}_{60}$  followed by oxidation

C <sub>60</sub>	H <sub>2</sub> O (1.0 eq) AlCl <sub>3</sub> (5 eq) arene (x eq)	Arh	H Ar 1) t-1 2) C	BuOK (2.4 eq) uBr∙SMe <sub>2</sub> (5 eq)	Ar Ar
-00	1,2-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	K		91–95%	
	28-52%	$\checkmark$	$\equiv$		
		1	la-d		2a-d
Entry	Arenes	1 x	Time (min)	Yield of <b>1</b> (%)	<b>2a-d</b> Yield of <b>2</b> (%)
Entry 1	Arenes Benzene ( <b>a</b> )	1 <i>x</i> 15	<b>a-d</b> Time (min) 270	Yield of <b>1</b> (%) 28 <sup>a</sup>	<b>2a-d</b> Yield of <b>2</b> (%) 95
Entry 1 2	Arenes Benzene ( <b>a</b> ) Toluene ( <b>b</b> )	1 x 15 10	Time (min) 270 60	Yield of <b>1</b> (%) 28 <sup>a</sup> 52	<b>2a-d</b> Yield of <b>2</b> (%) 95 92
Entry 1 2 3	Arenes Benzene ( <b>a</b> ) Toluene ( <b>b</b> ) 3,4-Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ( <b>c</b> )	1 x 15 10 10	<b>Time (min)</b> 270 60 120	Yield of <b>1</b> (%) 28 <sup>a</sup> 52 33	<b>2a-d</b> Yield of <b>2</b> (%) 95 92 94
Entry 1 2 3 4	Arenes Benzene ( $\mathbf{a}$ ) Toluene ( $\mathbf{b}$ ) 3,4-Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ( $\mathbf{c}$ ) Biphenyl ( $\mathbf{d}$ )	1 x 15 10 10 10	Time (min)        270        60        120        120	Yield of <b>1</b> (%) 28 <sup>a</sup> 52 33 28	<b>2a-d</b> Yield of <b>2</b> (%) 95 92 94 91

<sup>a</sup> 29% C<sub>60</sub>PhH was obtained.

<sup>b</sup> The reaction was conducted at 80 °C.



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were crucial to maximize the yield of the Friedel–Crafts reaction. The presence of excess water reduced the selectivity of the reaction and gave a complex mixture of inseparable products. With careful control of these variables in accordance with the reactivity of the arenes, the double hydroarylation reaction with benzene, toluene, o-xylene, and biphenyl was achieved to obtain the desired diaryldi-hydro[60]fullerenes,  $C_{60}Ph_2H_2$  (**1a**),  $C_{60}(4-MeC_6H_4)_2H_2$  (**1b**),  $C_{60}(3,4-Me_2C_6H_3)_2H_2$  (**1c**), and  $C_{60}(4-PhC_6H_4)_2H_2$  (**1d**) (Table 1). We obtained no trace of the desired product in the reaction with anisole, probably because of deactivation of the Lewis acid by anisole.

The bis-hydroarylated fullerene derivatives **1** were then dehydrogenated in one step to the desired diaryl[60]fullerenes **2**. After considerable experimentation, we found that a rather exotic combination of a base and an oxidant, <sup>t</sup>BuOK and CuBr·SMe<sub>2</sub>, afforded the desired product in an excellent yield (Table 1). Thus, <sup>t</sup>BuOK was the most suitable base among a variety of bases including KH, which was equally effective but more difficult to handle. CuBr or air, albeit less effectively, served as an oxidant in the second step. APCI-mass spectra indicated the molecular formulas of C<sub>60</sub>Ar<sub>2</sub> for these compounds, and the UV-vis spectra allowed us to distinguish between 1,2- and 1,4-diadducts,<sup>10</sup> because this class of compounds is known to exhibit a weak, but characteristic, broad absorption peak around 450 nm in the UV-vis spectra, as illustrated in Figure 1.

The symmetric diaryl[60]fullerene adducts **2** showed low solubility in common organic solvents; however, bearing a substituent on the phenyl rings, compounds **2b–d** showed moderate solubility in  $1,2-Cl_2C_6H_4$  (0.2–0.4 wt %), which made it possible to use in a solution process for the fabrication of a thin-film organic photovoltaic device. We therefore examined the LUMO levels of compounds **2b–d**.



Figure 1. UV-vis spectra of C<sub>60</sub> and 2d in 1,2-dichlorobenzene solution.



**Figure 2.** Cyclic voltammogram of **2d**. Measurement was performed in a 0.4 mM 1,2-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub> solution containing Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> (0.1 M) as a supporting electrolyte at 25 °C with a scan rate of 0.1 V/s.

Table	2		
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Reduction potentials	for $C_{60}$ , PCBM, and	1,4-diaryl[60]fullerenes <sup>a</sup>

Ar		$E_{1/2}^{\text{red}}$ vs. Fc/Fc <sup>+</sup>	LUMO level <sup>b</sup> (eV)	
	$E_1$ (V)	$E_2(V)$	$E_3$ (V)	
C <sub>60</sub> PCBM <b>2b</b> 2c 2d	-1.10 -1.18 -1.16 -1.17 -1.13	-1.49 -1.55 -1.55 -1.55 -1.55	-1.94 -2.05 -2.03 -2.03 -2.01	-3.70 -3.62 -3.64 -3.63 -3.67

<sup>a</sup> Potential in volts versus a ferrocene/ferrocenium couple was measured with cyclic voltammetry in  $1,2-Cl_2C_6H_4$  solution containing  $Bu_4N^+PF_6^-$  (0.1 M) as a supporting electrolyte at 25 °C with a scan rate of 0.1 V/s. Glassy-carbon, platinum wire, and Ag/Ag<sup>+</sup> electrodes were used as working, counter, and reference electrodes, respectively.

<sup>b</sup> The values of LUMO level were estimated using the following equation: LUMO level =  $-(4.8 + E_{1/2}^{tred})$  eV. See Ref. 11.

The diaryl[60]fullerene **2** undergoes reversible three-electron reduction as shown in Figure 2 at potentials characteristic of reduction of fullerene, indicating the formation of a monoanion, a dianion, and a trianion through reduction of the fullerene moiety. The reduction potentials and LUMO level are summarized in Table 2. The diaryl adduct **2** showed similar reductive potentials to PCBM, because both of them possess a  $58\pi$ -electron system. However, the present diaryl system allows us to tune the LUMO level by tuning the electronic properties of the aryl group. Thus, the alkyl groups (4Me and 3,4-Me<sub>2</sub>) in compounds **2b** and **2c** raised the LUMO level higher than that of **2d** (phenyl). This observation makes the diaryl[60]fullerene derivatives very attractive candidates as *n*-type semiconductors in solar cell research.

Finally, we evaluated the capacity of the diaryl[60]fullerene as an acceptor molecule in the *p-i-n* solution-processed OPV devices that we developed recently (tetrabenzoporphyrin (BP) as donor).<sup>2</sup> The active layer of the device was fabricated by spin coating to obtain the structure: indium tin oxide (ITO)/PEDOT:PSS/BP/BP:**2d**/**2d**/ bathocuproine (BCP)/Al. The pertinent photovoltaic properties are the following:  $V_{OC} = 0.63$  V,  $J_{SC} = 7.7$  mA/cm<sup>2</sup>, FF = 0.47, power conversion efficiency = 2.3%. The active layer of this OPV device exclusively utilizes aromatic compounds (i.e., BP and **2d**), which will result in a long life.

In summary, we have developed a concise synthesis of 1,4diaryl[60]fullerene adducts **2** by a unique combination of a Friedel–Crafts reaction and a Cu(I) mediated dehydrogenation. The solubility and the photophysical and electrochemical properties of these compounds suggested their utility in OPV devices, and this expectation was confirmed by the fabrication of a device that performs with 2.3% power conversion efficiency.

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#### Supplementary data

Supplementary data (synthetic procedures, NMR spectra, and device fabrication procedures) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet. 2011.01.031.

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- Synthesis of 1,4-bis(biphenyl)[60]fullerene (2d): ODCB (20 mL) containing water 9 (1.8  $\mu L,~0.01~mmol)$  was added to a mixture of  $C_{60}$  (72.1 mg, 0.1 mmol), aluminium(III) chloride (66.7 mg, 0.5 mmol), and biphenyl (154.2 mg, 1.0 mmol). The reaction mixture was stirred for 2 h at rt, before water (1 mL) was added. The dark-brown reaction mixture was diluted with CS2 and filtered through a short pad of silica gel. The dark-brown filtrate was evaporated to a small volume, and precipitation with MeOH afforded a crude product. This crude product was purified by column chromatography (eluent: CS2/ hexane = 2:1). Evaporation and precipitation with EtOH afforded  $C_{60}(4 PhC_6H_4)_2H_2$  (1d) (28.9 mg, 28% yield). To a solution of  $C_{60}(4-PhC_6H_4)_2H_2$ (25.7 mg, 0.025 mmol) in THF (10 mL) was added a solution of <sup>t</sup>BuOK in THF (60 µL, 0.06 mmol, 1 M) under an argon atmosphere. The color of the mixture changed immediately from dark brown to dark red. After the reaction mixture was stirred for 10 min at rt, CuBr SMe2 (25.7 mg, 0.125 mmol) was added. After stirring for 20 min at rt, the reaction mixture was diluted with toluene and filtered through a short pad of silica gel. The brown filtrate was evaporated to a small volume, and precipitation with MeOH afforded  $C_{60}(4-PhC_6H_4)_2$  (2d) (23.4 mg, 91% purity by HPLC) as a dark-brown solid.
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