

Organic photovoltaics incorporating fulleroisoquinolinones as n-type materials†

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Fulleroisoquinolinones have been synthesized by palladium-catalyzed annulation of *N*-alkyl benzamides with C₆₀. A device incorporating fulleroisoquinolinones and the conjugated polymer P3HT exhibited power conversion efficiency up to 2.3% under AM 1.5G irradiation.

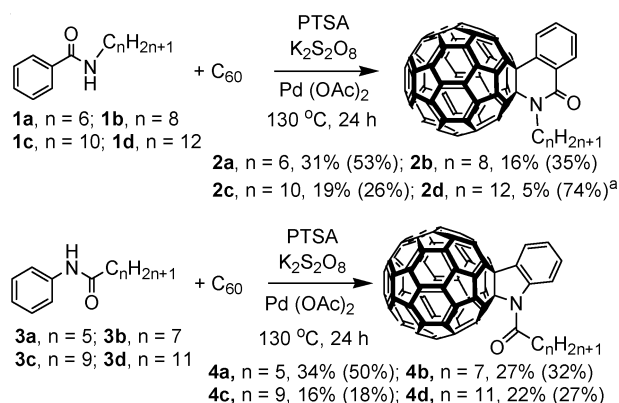
Demand for green and renewable energy is stimulating research into future materials for energy production. Solar energy technology is arguably the cleanest approach toward power generation. Thin films of materials possessing both electron accepting and donating functions play a unique role in solar energy technology because of their light weight, flexibility, and economical, low-temperature, and large-area fabrication.¹ Because fullerene derivatives² are good electron acceptors, they have become useful materials in thin film organic photovoltaics (OPVs).³ In particular, the commercialized fullerene derivative [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) is at present the mostly used n-type partner in studies of OPVs.⁴ With the innovation of material engineering, the power conversion efficiency (PCE) of OPVs has been improved over 6% using the blends of new conjugated polymers and PCBM.⁵ Endeavors on challenging higher PCE towards predicted theoretical limits are focused on the use of PCBM as n-type materials.⁶ However, only limited attempts have been made to develop new fullerene derivatives for OPV applications.

To date, some fullerene derivatives have been studied for OPV applications.⁷ Only few structurally similar fullerenes exhibit remarkable PCE when blended with conjugated polymers; for example, ThCBM displays a value of η comparable with that of PCBM (*ca.* 3.0%).⁸ Recently, Li *et al.* show that OPVs incorporating indene-C₆₀ bisadducts and P3HT exhibit higher PCE (6.5%) than those blended with PCBM.⁹ Since recent studies of OPVs have been heavily relied on PCBM, we think that developing new n-type materials remains an intriguing route for achieving higher PCE solar cells. Our interest in developing non-PCBM based derivatives for OPV applications led us to the synthesis of fulleroisoquinolinones and an exploration of their electrochemical properties and PV performances. It has been known that methanofullerenes tend to undergo ring opening upon one electron reduction. We

speculate that OPVs incorporating methanofullerenes as PCBM degrade through the ring opening process (retro-Bingel)¹⁰ upon long-term exposure to light.¹¹ The explored derivatives feature non-methanofullerenes that are relatively more stable for OPV applications. In this paper, we report palladium-catalyzed syntheses of fulleroisoquinolinones (6-member-ring) and fulleroindolines (5-member-ring) and evaluations of their performances when incorporated with P3HT in the device.

We efficiently prepared fulleroisoquinolinones **2a–d** and fulleroindolines **4a–d** in one step using palladium-catalyzed annulation of *N*-alkyl benzamides **1a–d** and anilides **3a–d** through C–H bond activation, respectively. Compounds **2a–b** were isolated in 5–31% yield (26–74% based on recovered C₆₀) and the yields for compounds **4a–d** are 22–34% (18–50% based on recovered C₆₀). We investigated long alkyl chains for improving their solubilities in organic solvents. We found that the reactions became low-yielding in all cases when longer alkyl chains were used. In particular, compound **2d** was not isolated under the standard conditions using *p*-toluene sulfonic acid (PTSA);¹² instead, we used 2,5-dimethylbenzoic acid as co-acids for achieving 5% yield of **2d** (Scheme 1).

We characterized the compounds **2a–d** and **4a–d** using infrared (IR) and ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy, and mass spectrometry. All MS data corresponded to the expected formulas of the isolated structures. Because each of these compounds possesses a symmetrical plane, its ¹³C NMR spectrum exhibits 30 sp²-hybridized carbon atoms on the C₆₀ cage. In their IR spectra, C=O stretching bands appear at *ca.* 1648–1651 cm⁻¹ for **2a–d** and *ca.* 1672–1674 cm⁻¹ for **4a–d**. The isolated compounds are generally brown in their solid states. They are generally soluble in CS₂, CHCl₃, CH₂Cl₂, chlorobenzene and *o*-dichlorobenzene.



^aWith 2,5-dimethylbenzoic acid as an acidic additive.

Scheme 1 (Yields in parentheses are based on recovered C₆₀.)

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We observed that compounds **2a–d** are higher in solubility than compounds **4a–d** in the above-mentioned solvents.

The electronic properties of the two structures **2a–d** and **4a–d** are revealed from their UV-vis spectral and electrochemical studies. Fig. S1 (ESI†) displays representative UV-vis spectra of compounds **2c**, **4c** and PCBM. The UV-vis absorption pattern was not influenced by their alkyl chain lengths, but by their annulation ring sizes or different functionalities (lactam vs. amide). We observed that the molar absorptivities in the visible region for compounds **2a–d** are generally slightly higher than those of **4a–d** taken in CHCl₃. In particular, the hump spanning from 660 to 700 nm is more intense exhibited by compound **2a–d**. It is noteworthy that PCBM displays relatively lower molar absorptivity from 400–550 nm in the visible region and an invisible hump from 660 to 700 nm as compared to that of **2c** (6-member-ring). The electronic absorption descends for **4c** at longer wavelengths.

Next, we used cyclic voltammetry (CV), differential pulse voltammetry (DPV), and Osteryoung square wave voltammetry (OSWV) to examine the redox properties of **2a–d** and **4a–d** for revealing any features in their electronic properties. Table 1 lists the half-wave reduction potentials of **2a–d** and **4a–d** relative to ferrocene/ferrocenium. We found that compounds **2a–d** are easier to be reduced than **4a–d** with *ca.* 40 mV anodic shifts; the first reductions for compounds **2a–b** are closer to that of C₆₀ and away from that of PCBM. In addition, the first reduction potential increases (less negative) slightly as the alkyl chains turn longer for compounds **2a–d** and those for compounds **4a–d** convert (more negative). Because the open circuit voltage (V_{oc}) is determined by the difference between the HOMO energy level of the polymers and the LUMO energy level of fullerenes, the higher LUMO levels (with more negative reduction potential) of the fullerene derivatives correspond to higher values of V_{oc} in the fabricated devices. Thus,⁵ we would expect that **4c** to exhibit the largest open-circuit voltage (V_{oc}) among the studied compounds.

We fabricated photovoltaic cells by spin-coating the blends from *o*-DCB solution. The OPVs with layered configuration of glass/ITO/PEDOT : PSS/P3HT : fullerenes (15 mg mL⁻¹ 1 : 1 w/w)/Ca/Al were fabricated using known methods.¹³ The performances of the P3HT/PCBM device under the same

Table 1 Half-wave reduction potentials (V)^a of C₆₀, PCBM, **2a–d**, and **4a–d**

Compound	E^1	E^2	E^3
C ₆₀	-1.13	-1.52	-1.98
PCBM	-1.21	-1.58	-2.08
2a	-1.16	-1.54	-2.00
2b	-1.15	-1.54	-2.02
2c	-1.14	-1.53	-2.02
2d	-1.14	-1.53	-2.00
4a	-1.18	-1.54	-1.94
4b	-1.19	-1.55	-1.95
4c	-1.20	-1.56	-1.95
4d	-1.19	-1.55	-1.95

^a Versus ferrocene/ferrocenium. Conditions: *ca.* 0.50 mM C₆₀, PCBM, **2a–d**, **4a–d** and 0.050 mM Bu₄NPF₆ in anhydrous *o*-DCB; reference electrode: Ag/0.01 M AgNO₃ and 0.050 mM (*n*-Bu)₄NClO₄ in anhydrous MeCN; working electrode: glassy carbon; auxiliary electrode: Pt; scanning rate: 50 mV s⁻¹.

Table 2 J - V characteristics of devices incorporating **2a–d**, **4d** and P3HT (1 : 1, w/w)

Entry	Compound	$J_{sc}/\text{mA cm}^{-2}$	V_{oc}/V	FF	PCE (%)
1	4d	2.6	0.40	0.55	0.6
2	2a	1.9	0.47	0.56	0.5
3	2b	3.0	0.45	0.54	0.8
4	2c	4.3	0.45	0.53	1.0
5	2d	3.0	0.39	0.55	0.6
6	2c ^a	5.1	0.49	0.59	1.5
7	2c ^b	6.2	0.51	0.66	2.1
8	2c ^c	7.0	0.51	0.65	2.3

^a Annealing at 140 °C. ^b Annealing at 160 °C. ^c Annealing at 180 °C.

experimental conditions were shown in ESI† for comparisons. Table 2 summarizes the performances of the OPV devices incorporating **2a–d**, **4d** and P3HT. Despite of their higher LUMO energy levels, the device performances based on **4a–d**/P3HT are dissatisfying since **4a–d** tend to aggregate into micro-domains during film formation and render them impossible to construct reasonable devices. We could only observe PCE of 0.6% while the **4d**/P3HT device was constructed by heating their blend solutions at 60 °C before active layer deposition (entry 1). In contrast to poor device performances with **4a–d**, compounds **2a–d** show promisingly better efficiency (entries 2–5). Among the **2a–d**-based devices, the **2c**/P3HT-based device displays the highest AM1.5G PCEs of 1% with V_{oc} of 0.45 V, J_{sc} of 4.3 mA cm⁻², and FF of 55.0%. To understand its causes, we employed AFM in the tapping mode through measurements of the topographies and phase diagrams of blend films. As shown in Fig. S2 and S3 (ESI†), larger aggregates and, thus, blend phase separation occurred in the devices with **4d**, **2a**, **2b** and **2d**. The root mean square (RMS) roughnesses were all higher than 5 nm. The relatively higher PCE of the **2c**-derived device appears to be related to its small phase separation domains (< 50 nm), which provided larger interfacial areas for exciton dissociation; as a result, its current density increased. The optimization of **2c**-derived devices was accomplished by thermal annealing before the vacuum deposition of electrode at different temperatures between 140–180 °C. As shown in Fig. 1, the thermal annealing has obvious effects on the OPV performances of the **2c**-derived devices. Annealing the active layer at different temperatures for 20 min (entries 6–8), the V_{oc} , J_{sc} ,

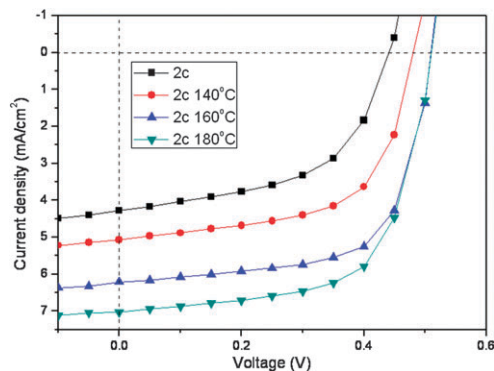


Fig. 1 J - V curves of **2c**/P3HT OPV devices with different annealing temperatures.

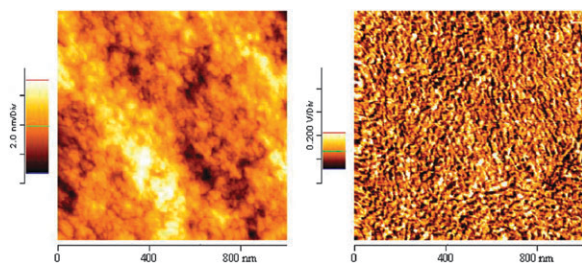


Fig. 2 Tapping-mode AFM ($1 \times 1 \mu\text{m}$) topography (a) and phase images (b) of the P3HT : **2c** blend film (1 : 1, w/w) annealed at 180°C for 20 min.

FF, and PCE of the device increased notably. The optimal PCE of 2.3% with significant improvements of J_{sc} and FF was obtained using annealing temperature at 180°C . AFM phase images of a two-component blend film provide clues regarding the surface hardness and the identity of the fullerene- and polymer-rich domains.^{13c,14} The phase image in Fig. S3 and S4 (ESI[†]) reveal two distinct feature types in the blend films: a dark-colored agglomerate, which we attribute to fullerene-rich domains, and bright regions, denoting the P3HT-rich domains. We find that the morphology of the blend film before thermal annealing is rough and the nanoscale phase segregation is relatively poor (Fig. S3 and S4 in ESI[†]). After annealing at 180°C , the blend film exhibits a morphology with well-separated P3HT and **2c** domains; the self-organized fibrillar feature of P3HT is clearly seen (Fig. 2). Thermal annealing results in enhanced degrees of P3HT crystallinity, improved nanoscale morphologies, and, consequently, improved device performances.

To conclude, we have efficiently synthesized non-PCBM based fullerisoquinolinones by Pd-catalyzed C–H activation and demonstrated the performance of OPV devices by using fullerisoquinolinones. We used a thermal treatment to achieve optimized bulk hetero-junction morphology. The device with PCEs up to 2.3% and high fill factor of over 65% were obtained. Further investigations to fine-tune the material energy bandgap and adjust V_{oc} toward higher PCE are currently underway.

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