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Bilayer- and bulk-heterojunction solar cells using liquid crystalline porphyrins as donors by solution processing

Qingjiang Sun and Liming Dai[a)]
Department of Chemical and Materials Engineering, University of Dayton, Dayton, Ohio 45469, USA

Xiaoli Zhou, Lanfang Li, and Quan Li[b)]
Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, USA

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Bilayer- and bulk-heterojunction solar cells based on liquid crystalline porphyrins (donors) were fabricated by solution processing. These porphyrins are (i) highly absorptive over the wavelengths of the solar spectrum, (ii) having energy levels matched well with the electron acceptors and anode materials to facilitate charge separation and transfer, and (iii) of a unique homeotropically aligned architecture for efficient charge transport and light harvesting. Thermal annealing of these solar cells induced alignments of porphyrins in the photoactive layers, leading to a factor of 4–5 higher power conversion efficiencies and short circuit current densities than their counterpart devices without postannealing. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2823586]

Semiconducting organic dye molecules[1,2] and conjugated polymers[3–6] have received considerable attention as promising photovoltaic materials in the next-generation solar cells.[7,8] In particular, recent studies[9,10] on organic photovoltaic cells (OPVs) based on certain environmentally stable organic molecules (e.g., polycrystalline Cu phthalocyanine) of high sunlight absorption efficiencies have shown energy conversion efficiencies up to ~5%, with much higher efficiencies being envisioned even for some flexible OPVs. Like the silicon-based photovoltaic cells,[7] however, the fabrication of OPVs often involves relatively expensive techniques associated with vacuum evaporation or vapor deposition. Furthermore, OPVs also often suffer from a low charge mobility as electrons/excitons may be scattered at grain boundaries associated with most of the organic molecules. Unfortunately, it is very difficult to obtain defect-free large single crystals of organic materials for photovoltaic applications. Therefore, the development of new solution-processable OPV materials with desirable photovoltaic properties could revolutionize the OPV technology.

The recent success on the synthesis of soluble liquid crystalline porphyrins[11,12] prompted us to develop solar cells based on these porphyrins that exhibit discotic liquid crystalline (LC) phases homotropically aligned into columns normal to the electrode surface to facilitate energy harvesting from sunlight. Furthermore, the homeotropically aligned liquid crystalline porphyrin donors with interposed C_{60} or 1-(3-methoxycarbonyl)propyl-1-phenyl-(6,6)C_{61} (PCBM) acceptors in bulk heterojunction devices should provide a large surface/interface for an efficient charge separation and a direct carrier transport to the electrodes through the aligned structure.

The LC porphyrins (C12Por and C14Por) were synthesized according to the published procedures.[11,12] Their chemical structures, as shown in Fig. 1, have been confirmed by ^{1}H NMR, ^{13}C NMR, MS, and elemental analysis. Their phase behaviors and the formation of columnar liquid crys-

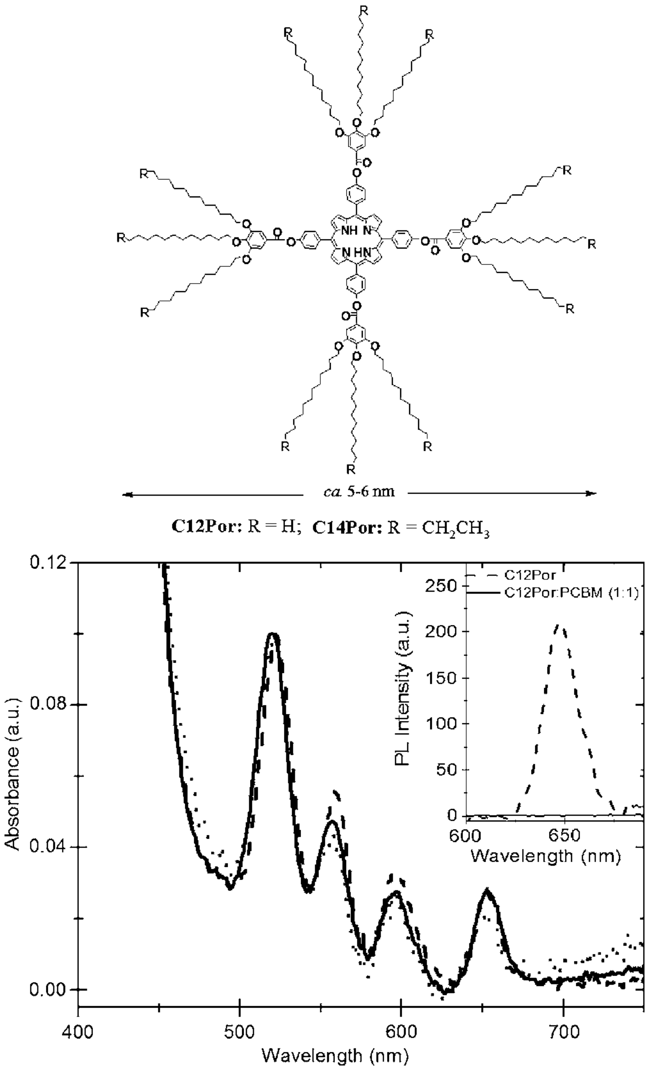

FIG. 1. Molecular structures of C12Por and C14Por (upper part) and optical absorption spectra (lower part) of as-prepared thin films (80–100 nm) of C12Por (solid line), C14Por (dash line), and an annealed C12Por film sandwiched between two quartz substrates (dot line). The inset shows the PL spectra of a thin film of C12Por and a blend film of C12Por with PCBM at a weight ratio of 1:1 excited at 520 nm.

[a)] Authors to whom correspondence should be addressed. Electronic mail: ldai@udayton.edu

[b)] Electronic mail: quan@lci.kent.edu

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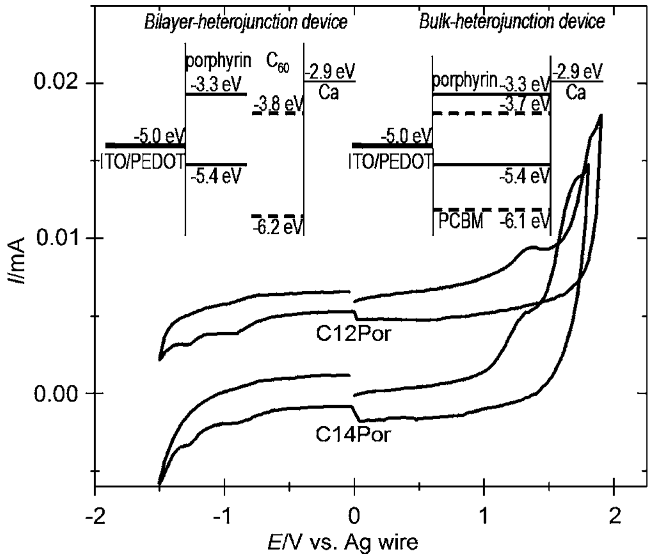

FIG. 2. Cyclic voltammograms of C12Por and C14Por thin films. The inset shows schematic energy level diagrams for porphyrins C_{60} and PCBM as well as typical electrode materials in both bilayer- and bulk-heterojunction devices.

talline phases were investigated by differential scanning calorimetry (DSC), polarizing optical microscopy, and synchrotron x-ray diffraction.[12]

Both bilayer- and bulk-heterojunction devices were fabricated with indium tin-oxide glass coated with 30-nm-thick poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) as anode and 15-nm-thick Ca capped with 150-nm-thick Al as cathode. In the bilayer solar cell, the active layer is composed of a porphyrin layer (80-nm-thick, spin-coated from its chlorobenzene solution) and a C_{60} layer (30-nm-thick, thermally deposited under vacuum). In the bulk-heterojunction device, a blend thin film of the porphyrin and PCBM (1:1 w/w and $\sim$(230–250)-nm-thick spin-coated from a chlorobenzene solution) was used as the active layer.

The optical absorption spectra for thin films of C12Por and C14Por are given in Fig. 1, which shows similar spectroscopic characteristics with strong absorption peaks at about 519, 557, 596, and 652 nm, respectively. The inset of Fig. 1 shows the photoluminescence (PL) spectra for a thin film of C12Por as well as a C12Por and PCBM (1:1 w/w) blend film (λ_{EX}=520 nm). The C12Por exhibited an emission peaked at approximately 648 nm with full width at half maximum of only 21 nm, whereas the deep-red emission of porphyrin was fully quenched upon blending with PCBM due to an efficient electron transfer from porphyrin to PCBM in the blend system.

To determine the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels, cyclic voltammetry was carried out for C12Por and C14Por thin films. Figure 2 shows similar cyclic voltammograms with two oxidation peaks at approximately 1.36 and 1.82 V, and one reduction peak at −1.26 V, having the onset potentials for the first oxidation (E'_{ox}) and reduction (E'_{red}) at approximately 1.0 and −1.1 V versus Ag wire, respectively, for both C12Por and C14Por. The HOMO and LUMO levels of C12Por and P14Por were calculated to be −5.4 and −3.3 eV, respectively, according to equations HOMO$=-(E'_{ox}+4.39\text{ eV})$ and LUMO$=-(E'_{red}+4.39\text{ eV})$.[13] Because the HOMO and LUMO levels of the porphyrins are 0.7/0.8 and 0.4/0.5 eV higher than those of PCBM/C_{60} (the inset of Fig. 2), the porphyrins act as donors with respect to PCBM (or C_{60}).

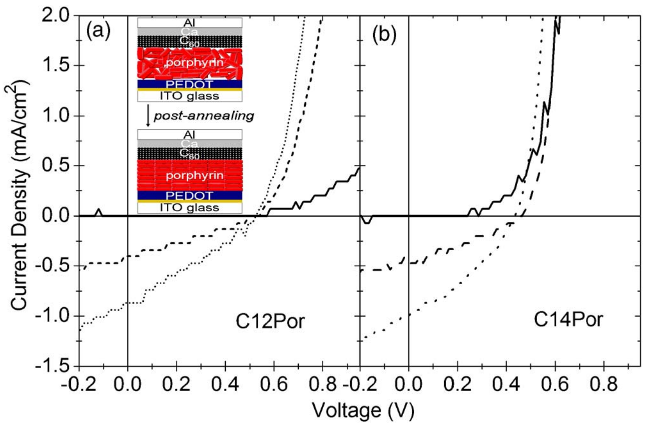

FIG. 3. (Color online) J-V characteristics of the bilayer solar cells based on (a) C12Por and (b) C14Por under dark (solid line), and before (dash line) and after (dot line) postannealing under the illumination of AM 1.5 G and 100 mW/cm^2. The inset of (a) schematically shows possible ordering in the porphyin-based bilayer-heterojunction solar cell by postannealing.

Figures 3(a) and 3(b) show current density versus voltage (J-V) characteristics for bilayer solar cells based on C12Por and C14Por, respectively, before and after a postannealing under the illumination of AM 1.5G and 100 mW/cm^2. The *as-prepared* C12Por-based solar cell exhibited an open circuit voltage (V_{oc}) of 0.495 V, a short circuit current density (J_{sc}) of 0.400 mA/cm^2, and a power conversion efficiency (PCE) of 0.070%. The relatively poor performance of the bilayer device was attributable to the limited interfacial area between the donor and acceptor layers, where electron-hole separation occurred.[3] Hole hopping[14,15] is also difficult in the nonaligned liquid crystalline porphyrin layer due to the presence of voids, grain boundaries, and interstitial spaces. With an increased C–C linkage chain length, the V_{oc} of the as-prepared C14Por-based device decreased to 0.450 V with respect to the C12Por-based device, whereas the corresponding J_{sc} increased to 0.470 mA/cm^2, attributing to the reduced recombination losses of the "excitons/carriers" through an enhanced charge localization in the C14Por device, as is the case for the donor-bridge-acceptor type block copolymer systems.[16,17]

Our DSC and X-ray diffraction data[11,12] indicated that the two porphyrins have the similar phase sequence of isotropic, hexagonal LC phase, ordered hexagonal LC phase, and crystalline phase. By heating the devices from room temperature to $\sim$140 °C to make porphyrins into isotropic phase and holding for $\sim$10 min, followed by sequentially cooling down from 140 to 80 °C with an average cooling rate of 0.2 °C/min and from 80 °C to room temperature with a cooling rate of 5 °C/min, we performed the postannealing for both the C12Por and C14Por based bilayer devices. Figure 3 shows that the postannealing indeed induced a more than 100% increase in both J_{sc} (C12Por: 0.400−0.870 mA/cm^2; C14Por: 0.470−1.010 mA/cm^2) and PCE (C12Por: 0.070−0.141%; C14Por: 0.069−0.151% , presumably due to the thermally induced alignment of porphyrin layer.[12] The homeotropic alignment of the porphyrins could not only provide the most efficient pathway for hole conduction along the columnar axis, but also offer the largest area to the incident light for optimized light harvesting. Unlike the

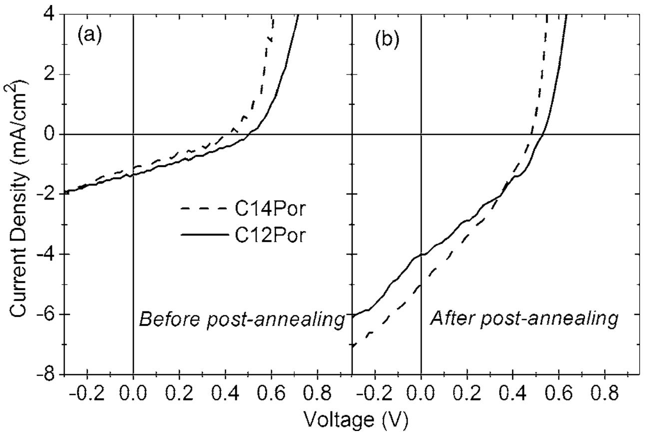

FIG. 4. *J-V* characteristics of the bulk-heterojunction solar cells based on C12Por and C14Por (a) before and (b) after postannealing under the illumination of AM 1.5 G and 100 mW/cm^2.

polythiophene-based solar cells with which the postannealing was demonstrated to enhance the long-wavelength absorption due to the extended conjugation through thermal rearrangement of polymer chains,[18,19] however, the thermal annealing of C12Por or C14Por did not broaden the absorption features of porphyrins (see Fig. 1) as the conjugation length along the cross section of the homeotropically-aligned columns, if any, remained unchanged.

Figures 4(a) and 4(b) show *J-V* characteristics for the bulk-heterojunction solar cells based on C12Por and C14Por before and after the postannealing, respectively. Compared to the bilayer devices, the bulk-heterojunction solar cells showed much improved performance because of the maximized interfacial area for the charge separation and collection. In particular, the as-prepared C12Por-based bulk-heterjounction solar cell exhibited a V_{oc} of 0.510 V, J_{sc} of 1.340 mA/cm^2, and PCE of 0.222%. Unlike the bilayer devices, however, the V_{oc}, J_{sc}, and PCE of the bulk-heterojunction devices decreased with increasing C–C linkage chain length from C12Por to C14Por (V_{oc}=0.43 V; J_{sc}=1.140 mA/cm^2; PCE=0.155%). This is because charge localization in the bulk-heterojunction devices is difficult, if not impossible, as electrons can transfer from porphyrin to adjacent PCBM in the blend photoactive layer. Nevertheless, the distance over which electrons need to transfer from porphyrin to PCBM increases with increasing C–C linkage chain length, and hence the decreased performance for the C14Pro-based bulk device was observed.

As shown in Figs. 4(a) and 4(b), J_{sc}s and PCEs of the bulk-heterojunction solar cells were also improved significantly with about 200%–300% and 300%–400% increase, respectively, by the postannealing treatment due, once again, to the thermally induced alignment of the porphyrins—though a full homeotropic alignment may be difficult in the blend system with PCBM interdispersed between the porphyrin liquid crystal columns. After the postannealing, the C12Por-based device achieved a J_{sc} of 3.990 mA/cm^2 and a PCE of 0.712%, while the C14Por-based device exhibited a J_{sc} of 5.02 mA/cm^2 and a PCE of 0.775%. Despite the better performance achieved for the as-prepared C12Por-based bulk device than its C14Por counterpart, the higher J_{sc} and PCE for the *postannealed* C14Por-based solar cell than those of its C12Por counterpart may well indicate a better thermally-induced alignment of C14Por than C12Por in the active layers.

In summary, we have fabricated the bilayer- and bulk-heterojunction solar cells using liquid crystalline porphyrins as donors by solution processing. Postannealing was shown to improve the performance significantly for both the bilayer- and the bulk-heterojuncton solar cells due to the alignments of porphyrins. After postannealing, the bulk-heterojunction devices achieved the PCEs up to 0.775% and the J_{sc}s up to 5.020 mA/cm^2 under a radiation of 100 mW/cm^2. This study provides a solution processing and postannealing approach to efficient, and even flexible, porphyrin-based OPVs with the desired donor/acceptor blend architectures and morphologies at macro and nanoscales.

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