Effects of Magnetic Nanoparticles and External Magnetostatic Field on the Bulk Heterojunction Polymer Solar Cells

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The price of energy to separate tightly bound electron-hole pair (or charge-transfer state) and extract freely movable charges from low-mobility materials represents fundamental losses for many low-cost photovoltaic devices. In bulk heterojunction (BHJ) polymer solar cells (PSCs), approximately 50% of the total efficiency lost among all energy loss pathways is due to the photogenerated charge carrier recombination within PSCs and low charge carrier mobility of disordered organic materials. To address these issues, we introduce magnetic nanoparticles (MNPs) and orientate these MNPs within BHJ composite by an external magnetostatic field. Over 50% enhanced efficiency was observed from BHJ PSCs incorporated with MNPs and an external magnetostatic field alignment when compared to the control BHJ PSCs. The optimization of BHJ thin film morphology, suppression of charge carrier recombination, and enhancement in charge carrier collection result in a greatly increased short-circuit current density and fill factor, as a result, enhanced power conversion efficiency.

In recent years, bulk heterojunction (BHJ) polymer solar cells (PSCs) composed of conjugated polymers (as the electron donor, D) and fullerene derivatives (as the electron acceptor, A) with interpenetrating networks have attracted a myriad of attention for both academic and industrial sectors due to their premium features of flexibility, fabrication simplicity, low manufacturing costs, short energy payback time, and low environmental impact. In the past few years, progresses have mainly focused on breaking the Shockley-Queisser limit by ameliorating device structures and developing novel low bandgap conjugated polymers. Power conversion efficiencies (PCEs) over 10% from single junction cells and as high as 12% from the tandem cells have been reported. However, the fundamental question regarding energy losses during the photophysical process still remain obscure; particularly, the mechanisms of charge carrier recombination in BHJ PSCs are far from elucidated.

As shown in Fig. 1, the charge carrier collection in BHJ PSCs includes the following steps/processes: formation of photo-induced excitons in D and A, respectively; intra-molecular electron-hole recombination; the excitons diffusion and dissociation at the D/A interface; charge-transfer (CT) states generation and then dissociation into free charge carriers (electrons and holes) with an ultrafast quasi-adiabatic charge transfer process; charge carriers that are transported through either D or A and then being collected by the respective electrodes; the separated charge carriers may recombine with each other (7, geminate recombination) before dissociation; moreover, the separated charge carriers may also being collided and recombined (8, bimolecular recombination or non-geminate recombination) before collected by the respective electrodes. The germinate and non-germinate recombinations are certainly responsible for the low PCEs in BHJ PSCs. On the other hand, the relative dielectric constant ($\varepsilon_r$) of BHJ composite in PSCs is as low as 3, which is much smaller than that of typical inorganic counterparts (~10). The small dielectric constant results in strongly bounded Frenkel excitons with a diffusion length of ~10 nm for organic semiconductors rather than the Wannier excitons for inorganic semiconductors with a diffusion length of $10^5$ nm. Thus, in order to efficiently dissociate the photo-excited excitons in BHJ composite of PSCs, optimal phase separation with ~10 nm scale is required. However, it is not easy to form a uniformly ideal ~10 nm interpenetrating phase separation in BHJ composite. As a result, most high efficiency PSCs were obtained by optimization of BHJ thin film morphology through huge processing effects. In addition, the traps and defects in BHJ composite also play a crucial role in exciton recombination. Therefore, the challenge in forming uniformly ideal ~10 nm interpen-
etrate A–D phase separation and traps defects therein together
with the low $\varepsilon_r$ of disordered organic materials induced various
recombinations are responsible for approximately 50% efficiency
loss among all loss pathways in BHJ PSCs 15,16.

Studies from the transient photoconductivity, the time-delayed
collection field, and the time-delayed dual pulse experiments have
demonstrated that there is a competition process between the
carrier sweep-out by the internal field and the loss of photogenerated car-
riers by recombination in BHJ PSCs 17. Wherein the internal electric
field with a value as high as 50 to 70 V/\mu m is required to ensure
efficient charge collection at the short-circuit condition and in
reverse bias in PSCs 18,19. The asymmetrical electrode materials used
in most of BHJ PSCs, however, afford a work-function difference of
less than 2 eV producing an external electric field of $\sim$20 V/\mu m
(assuming the BHJ thickness is $\sim$100 nm for typical device dimen-
sions). This electric field is less efficient to sweep out photogenerated
 carriers and suppress charge carrier recombination in BHJ active
layer19,20. Considering the insufficient electric field from the electro-
des discussed above, a coercive electric field from magnetic nano-
particles (MNP) show potential to strengthen the external electric
field in BHJ PSCs.

In MNP s, a coercive electric field is produced among MNP s due to
dipole interactions21. If the BHJ composite is incorporated with
MNP s and then followed with an external magnetostatic field align-
ment, an orientated coercive electric field ($E$) will be created within
BHJ composite (see in Fig. 2G). The $E$ is described as: $E = (4\pi\alpha/\varepsilon \sigma f)$22–24, where $\varepsilon$ is the dielectric permittivity, $\sigma$ is the surface
charge density and $f$ is the volume fraction of MNPs. For example, an
additional $E$ of 177.4 V/\mu m, which is at least 2 times larger than 50–
70 V/\mu m, can be obtained by BHJ composite incorporated with 5% (by volume) of Fe$_3$O$_4$ MNPs. The details in calculation of $E$
is described in Supplementary Information (SI 1). This additional coer-

**Figure 1** The operational principle of bulk-heterojunction polymer solar
cells: formation of photo-induced excitons in D and A, respectively
(1 & 1'); intra-molecular electron-hole recombination (2 & 2'); the
excitons diffusion and dissociation at the D/A interface (3 & 3');
generation of charge-transfer (CT) states and these CT states dissociate
into free charge carriers (electrons and holes) with an ultrafast quasi-
adiantic charge transfer process (4 & 4'); charge carriers that are
transported through either D or A (5 & 5') and then collected by the
respective electrodes (6 & 6'); the separated charge carriers may recombine
with each other (7, geminate recombination) before dissociation;
the separated charge carriers may also collide and be recombined
(8, bimolecular recombination or non-geminate recombination) before
being collected by the respective electrodes (6 & 6').

**Figure 2** (A) The molecular structures of PTB7-F20 and PC$_{71}$BM; (B) the conventional device structure of PSCs without incorporating any Fe$_3$O$_4$
magnetic nanoparticles (MNPs); (C) the conventional device structure of PSCs incorporated with Fe$_3$O$_4$ MNPs and aligned by an external magnetostatic
field; (D)–(F) the fabrication procedures of PSCs incorporated with Fe$_3$O$_4$ MNPs and aligned by an external magnetostatic field; (D) BHJ active layer
incorporated with Fe$_3$O$_4$ MNPs was spin-coated on PEDOT:PSS coated ITO substrate; (E) a ferromagnet was suspend above the surface of BHJ composite
incorporated with Fe$_3$O$_4$ MNPs layer. The magnetic intensity is $\sim$30–40 G and the distance between the ferromagnet and BHJ composite layer is $\sim$10 cm;
(F) oriented Fe$_3$O$_4$ MNPs inside BHJ active layer by an external magnetostatic field. In pre-devices; (G) Drawing of partial enlargement of Fe$_3$O$_4$ MNP in
(C), showing an antiparallel relation between the magnetic dipole (caused by the Fe$_3$O$_4$ crystal inside the particle) and electric dipole (caused by the
difference of charge density between the inside Fe$_3$O$_4$ and outside organic coater).
cive electric field is expected to enlarge the sweep-out rate of photogenerated carriers and suppress charge carrier recombination (both geminate and non-geminate); consequently resulting in enhanced PCEs in BHJ PSCs. In addition, these MNPs are also expected to influence the formation of thin film morphology of BHJ composite due to the motion of these MNPs under an external magnetostatic field\(^3\).

The \(v_0\) of Fe\(_3\)O\(_4\) MNPs is 20, which is 5 times higher than that of BHJ composite (4) \((v_0, \text{of ~poly(3-hexylthiophene) (P3HT) is } 6.5\) and \(v_0\) of phenyl-c61-butyric-acid-methyl ester (PC\(_{61}\)BM) is 3.9, the \(v_0\) of P3HT:PC\(_{60}\)BM BHJ composite is assumed to be \(-4\)\(^3\). The average \(v_r\) of BHJ composite incorporated with 5% (by volume) Fe\(_3\)O\(_4\) MNPs can be enlarged by a factor of 20\(^3\). Consequently, the Coulomb potential energy \(E_C = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r}\) (where \(e\) is the charge of an electron, \(\varepsilon_r\) is the relative dielectric constant of the surrounding medium, \(\varepsilon_0\) is the vacuum permittivity, and \(r\) is the electron-hole separation distance) of the CT state could be reduced due to enlarged \(v_0\) and optimized \(r\) (due to optimized BHJ film morphology). Moreover, the reduced \(E_C\) will enlarge the total energy \(U\) of the CT state since the \(U\) is described as\(^26\):

\[
U = |E_D(\text{HOMO}) - E_A(\text{LUMO})| - E_C + \frac{1}{2} m_e V_e^2 + \frac{1}{2} m_h V_h^2
\]

where \(E_D(\text{HOMO})\) and \(E_A(\text{LUMO})\) are the HOMO (highest occupied molecular orbital) energy level of D and the LUMO (lowest unoccupied molecular orbital) energy level of A; \(V_e\) and \(V_h\) are the electron and hole drifting velocities, respectively; \(m_e\) and \(m_h\) are the masses for electron and hole, respectively. In the eq. (1), the kinetic energies \(\left(\frac{1}{2} m_e V_e^2\right)\) and \(\left(\frac{1}{2} m_h V_h^2\right)\) of charge carriers are increased due to the introduction of Fe\(_3\)O\(_4\) MNPs dipole-induced coercive electric field, which is an additional electric field to drive the separated charge carriers to be transported through either D or A. As a result, decreased \(E_C\) and increased kinetic energy would result in an enlarged \(U\) of the CT state. Therefore, it is unequivocal that the CT state becomes unstable which would facilitates the charge carrier dissociation\(^28\) resulting in an enlarged short-circuit current density \(J_{SC}\) in PSCs\(^27,28\). Moreover, the direction of the dipolar moment produced by Fe\(_3\)O\(_4\) MNPs is parallel in the presence of the vertically external magnetostatic field\(^29,30\). This parallel alignment could force Fe\(_3\)O\(_4\) MNPs to be temporarily bound with the separated charge carriers in "ordered" structures, which facilitates the charge carrier to be transported to the respective electrodes (see Fig 2F & 2G and Fig 4D). Therefore, the PSCs based on BHJ composite incorporated with Fe\(_3\)O\(_4\) MNPs and then followed with a vertical external magnetostatic field alignment are expected to possess enhanced PCEs.

In order to verify above hypothesis, the PSCs fabricated by various BHJ composites, which are incorporated with Fe\(_3\)O\(_4\) MNPs and then followed with an external magnetostatic field alignment, are investigated. The device architecture of PSCs is ITO/PEDOT:PSS/BHJ active layer/Ca/Alumnum, where ITO is indium tin oxide, PEDOT:PSS is poly(ethylenedioxythiophene):poly(styrenesulfonate), BHJ active layer is BHJ composite incorporated with Fe\(_3\)O\(_4\) MNPs. Here, we only report PSCs fabricated by PTB7-F20:PC\(_{71}\)BM BHJ composite blended with 5% v/v Fe\(_3\)O\(_4\) MNPs; the PSCs fabricated by other BHJ composites incorporated with Fe\(_3\)O\(_4\) MNPs and the influence of Fe\(_3\)O\(_4\) MNPs on the performance of PSCs are described in SI 2, SI 3 and SI 5. PFB7-F20 is fluorinated copolymer based on thiieno[3,4-b]thiophene copolymer with 20% fluorene unit\(^28\) and PC\(_{71}\)BM is phenyl-C\(_{71}\)-butyric acid methyl ester. The molecular structures of PFB7-F20 and PC\(_{71}\)BM are shown in Fig. 2A. The fabrication of PSCs incorporated with Fe\(_3\)O\(_4\) MNPs is described in Figs. 2D to 2F and Fig. 2C (also SI 3). The device fabrication and characterization are described in experimental section. Fig. 2G illustrates that the direction of magnetic dipoles by Fe\(_3\)O\(_4\) MNPs and the electric dipoles by an external electric field is in an antiparallel pattern. PSCs based on BHJ composite incorporated with Fe\(_3\)O\(_4\) MNPs and then aligned by an external magnetostatic field alignment (represent as the PSCs-Fe\(_3\)O\(_4\) W/H). PSCs based on BHJ composite incorporated with Fe\(_3\)O\(_4\) MNPs without any external magnetostatic field alignment (represent as the PSCs-Fe\(_3\)O\(_4\) W/O). Evidently, Fe\(_3\)O\(_4\) MNPs are randomly distributed in BHJ-Fe\(_3\)O\(_4\) while Fe\(_3\)O\(_4\) MNPs are aligned in certain orders in BHJ-Fe\(_3\)O\(_4\) W/H. These aligned Fe\(_3\)O\(_4\) MNPs are solely due to the magnetic dipole interaction\(^21,23\). Due to the magnetically and electrically anisotropic properties of Fe\(_3\)O\(_4\) MNPs, e.g. Fe\(_3\)O\(_4\) Janus particles\(^28\), the coercive
electric field within Fe₃O₄ MNPs can be constrained in vertically direction by means of magnetically induced rotation and alignment of Fe₃O₄ MNPs, which originate from the magnetic dipole direction within an external magnetostatic field. This coercive electric field makes Fe₃O₄ MNPs to be temporarily bound with the separated charge carriers in the ordered directions, which facilitates separated charge carriers to be transported to the respective electrodes. As a result, high PCEs and IPCEs are observed from the PSCs-Fe₃O₄ and the PSCs-Fe₃O₄ W/H.

GISAXS is further carried out to characterize the structural features with d-spacing on the domain size level (long range) in BHJ thin layer. Figs. 5A & 5B present the GISAXS patterns at the incident angle of 0.2° for BHJ-Fe₃O₄ and BHJ-Fe₃O₄ W/H and Fig. 5C presents the fitting curve of GISAXS pattern of BHJ-Fe₃O₄ W/H. The GISAXS patterns of BHJ composite and BHJ-Fe₃O₄ are almost identical and do not have any distinctive in-plane order, which indicate a random distribution of Fe₃O₄ MNPs inside BHJ active layer. However, in BHJ-Fe₃O₄ W/H, a diffraction peak along Q_y direction is located at 0.08 Å⁻¹, which indicates an ordered, self-assembled Fe₃O₄ MNPs was formed (see Fig. 5B). Moreover, the value of 0.08 Å⁻¹ corresponds to an interparticle spacing of \( \frac{2\pi}{Q_y} \approx 76.6 \text{ Å} \), where Q_y is a component of scattering vector. It is apparent that Fe₃O₄ MNPs were orientated in a certain orders within the BHJ interpenetrating network due to an external magnetostatic field alignment. Moreover, by controlling the kinetic alignment of Fe₃O₄ MNPs within BHJ composite, the thermodynamics of the D-A interpenetrating network should be affected, consequence, as shown in SI Fig. S8, the BHJ-Fe₃O₄ W/H active layer shows premium morphology with more exquisite D-A separation of a uniform scale of ~10 nm, ensuring sufficient exciton dissociation. This refined phase-separation dimension indicates a larger interfacial area.
for efficient charge generation. In short, the magnetically induced film morphology rearrangement leads to an ordered and nanoscale optimized interpenetrating network, which facilitates charge carriers to be transported to the respective electrodes, simultaneously reduces the possibility of charge carrier recombination\(^{36–38}\). As a result, enhanced PCEs are observed from PSCs-Fe\(_3\)O\(_4\) W/H.

The photo-electronic characteristics of PSCs are further investigated to confirm the effect of coercive electric field on charge generation efficiency. Fig. 6A shows the photocurrent (\(J_{\text{ph}}\)) versus the effective voltage (\(V_{\text{eff}}\)) characteristics of PSCs under AM 1.5 G illumination. At a large reverse voltage (\(V_{\text{eff}} = 1.9\) V), \(J_{\text{ph}}\) is saturated for three different PSCs, suggesting that the photogenerated excitons are dissociated into free charge carriers and these charge carriers are collected by the electrodes without any residual non-geminate recombination\(^{36–38}\). As a result, the saturation current densities (\(J_{\text{sat}}\)) are only dependent upon the amount of absorbed incident photon flux\(^{36}\). The maximum obtainable exciton generation rates are essentially the same for all three types of PSCs because the Fe\(_3\)O\(_4\) MNPs contributed negligible absorption to BHJ composite (SI 4, Fig. S3). At \(V_{\text{eff}} = V_{\text{OC}}\) (\(V_{\text{OC}} = 0.65\) V), the \(J_{\text{ph}}/J_{\text{sat}}\) are 92.2%, 91.6% and 88.8% (\(J_{\text{sat}}\) is the reverse saturation photocurrent at \(V_{\text{eff}} = -1.9\) V) for the PSCs-Fe\(_3\)O\(_4\) W/H, the PSCs-Fe\(_3\)O\(_4\), and the control PSCs, respectively. Interestingly, in the low effective voltage range, i.e. \(V_{\text{eff}} < 0.5\) V, \(J_{\text{ph}}/V_{\text{eff}}\) characteristics of these three types PSCs show distinct differences. At the maximum power output condition at \(V_{\text{eff}} = 0.2\) V, \(J_{\text{ph}}/J_{\text{sat}}\) are 84.6%, 83.1% for the PSCs-Fe\(_3\)O\(_4\) W/H and the PSCs-Fe\(_3\)O\(_4\) while it is only 78.7% for the control PSCs. Since the ratio of \(J_{\text{ph}}/J_{\text{sat}}\) is the essential of exciton dissociation efficiency and charge carrier collection efficiency, a decreased \(J_{\text{ph}}/J_{\text{sat}}\) suggests either reduced exciton dissociation efficiency or decreased charge carrier collection efficiency. The decreased charge carrier collection efficiency suggests that non-geminate recombination is dominated (compete over exciton-dissociation), resulting in a low FF. The charge carrier recombination in PSCs is manifested by the deviation of the photocurrent from the square-root dependence on effective voltage, which is one of the signatures of charge carrier recombination-limited photocurrent in PSCs\(^{36–38}\). The superior \(J_{\text{ph}}\), \(V_{\text{eff}}\) characteristics from the PSCs-Fe\(_3\)O\(_4\) W/H clearly demonstrate the effect of Fe\(_3\)O\(_4\) MNPs and external magnetostatic field alignment on reducing the geminate recombination at the low effective voltage, at which maximum power output condition of PSCs usually takes place. Such reduced geminate recombination in PSCs is probably originated from high charge carrier mobility of BHJ composite therein. Therefore, the enhancement in charge carrier diffusion and charge carrier transport are responsible for the distinctly different \(J_{\text{ph}}/J_{\text{sat}}\) among all PSCs.

Light intensity-dependent efficiencies (\(J_{\text{SC}}\) and \(V_{\text{OC}}\)) were further studied to confirm the effect of the coercive electric field on suppression of geminate and non-geminate recombinations in PSCs. In solar cells, if the mean drift length of the electron or hole (or both) is smaller than the thickness of photoactive layer, geminate recombination becomes considerable. Figs. 6B & 6C represent the steady-state light-intensity dependence of \(J_{\text{SC}}\) and \(V_{\text{OC}}\) for all PSCs. The PSCs-Fe\(_3\)O\(_4\) W/H exhibits a near-linear dependence of \(J_{\text{SC}}\) with the light intensity, and a coefficient of \(\alpha = 0.99\) corresponding to the power law \(J_{\text{SC}} \propto I^\alpha\), where \(I\) is the light intensity. Both the PSCs-Fe\(_3\)O\(_4\) and the control PSCs show slightly non-linear characteristics of \(J_{\text{SC}}\) versus \(I\) with a coefficient of \(\alpha = 0.95\) and \(\alpha = 0.92\), respectively. The different \(\alpha\) values indicate that non-geminate recombinations are different in these three types of PSCs. The nearly linear dependence of \(J_{\text{SC}}\) is consistent with sweep-out at short circuit; however, this also indicates that non-geminate recombination is relatively weak\(^{37}\).
When PSCs are measured under illumination at open circuit voltage, the applied voltage equals to the difference between the quasi-Fermi-levels within the polymer and fullerene phase separated domains. The relations between $V_{OC}$ and light intensity can be described as $V_{OC} = S \ln(I)$, where $S$ is the slope and $I$ is the light intensity. The fits for the PSCs-Fe$_3$O$_4$ W/H, the PSCs-Fe$_3$O$_4$ and the control PSCs are shown in Fig. 6C. The slope of $S = 0.028$, which is close to the value of $kT/q (0.026)$, is observed from the PSCs-Fe$_3$O$_4$ W/H. This observation is consistent with the predictions of a drift-diffusion model with constant quasi-Fermi levels throughout the PSCs, indicating the geminate recombination is significantly suppressed in the PSCs-Fe$_3$O$_4$ W/H. The slope of $S = 0.032$ is observed from the PSCs-Fe$_3$O$_4$, suggesting an alleviated geminate recombination compared with the control PSCs whose slope is 0.034.

In PSCs, due to the low charge carrier mobility of disordered organic materials, charge carrier recombination becomes the dominant loss mechanism as the thickness of BHJ active layer increases. Fig. 6D presents PCEs versus the thickness of BHJ active layer. It was found that as the thickness of BHJ thin films increases from 120 nm to 260 nm, the PCEs from the control PSCs are significantly decreased from 5.2% to 4.5%; however, the PCEs from the PSCs-Fe$_3$O$_4$ decreased from 5.8% to 5.4%; while the PCEs from the PSCs-Fe$_3$O$_4$ W/H maintained almost the same value, around 7.0%. These results demonstrate that Fe$_3$O$_4$ MNPs and an external magnetostatic field alignment can suppress the charge carrier recombination in the PSCs based on BHJ composite incorporated with Fe$_3$O$_4$ MNPs and then followed by an external magnetostatic field alignment.

In BHJ PSCs, the built-in electric field can be canceled at the condition of applied bias voltage ($V_{appl}$) equals to $V_{OC}$; at this condition, the photogenerated charge carriers in the active layer flowing toward the electrodes can be prevented. As a result, the possibility of charge recombination at the D/A interface is increased to the maximum value. The impedance spectroscopy (IS) is carried out to monitor the detailed electrical properties of BHJ composite and/or the interface between each layer that cannot be observed by direct current measurement. The details of IS measurement is described in SI 7. In all PSCs, the difference in the resistance of PSCs solely comes from the CT resistance with BHJ composite active layer. Fig. 7 shows the Nyquist plot of PSCs at $V_{appl} = V_{OC}$ and under 100 mW/cm$^2$ from AM 1.5 G illumination. The plot of PSCs contains a semicircle which indicates that BHJ active layer is relatively homogeneous along the transport pathways without having discernible multiple interfacial boundaries. At $V_{appl} = V_{OC}$, the CT resistance of the control PSCs is $\sim 83 \ \Omega$ and this value decreases to $\sim 58 \ \Omega$ and $\sim 32 \ \Omega$ for the PSCs-Fe$_3$O$_4$ and the PSCs-Fe$_3$O$_4$ W/H, respectively. A significantly decreased CT resistance demonstrates that thin film morphologies are rearranged through PTB7-F20 crystallization and/or PC$_7$BM aggregation, which enhances the charge carrier transport and decreases the possibility of charge carrier recombination at the D/A interface in BHJ active layer. These observations are consistent with the film morphologies presented in AFM images (SI 6, Figure 5 | Grazing-incidence small-angle scattering (GISAXS) pattern at the incident angle of 0.2° for (A) BHJ composite incorporated with Fe$_3$O$_4$ magnetic nanoparticles (MNPs) without any external magnetostatic field treatment and (B) BHJ composite incorporated with Fe$_3$O$_4$ MNPs and followed with an external magnetostatic field alignment. (C) Fitting curve of GISAXS pattern of BHJ composite incorporated with Fe$_3$O$_4$ MNPs and followed with an external magnetostatic field alignment.
Fig. S8) and are in good agreement with our hypothesis that an external magnetostatic field alignment can force Fe₃O₄ MNPs to create temporary “channels” for transporting separated charge carriers to the respective electrodes.

Based on space charge limited current (SCLC) method, charge carrier mobilities of PTB7-F20 and PC₇₁BM are investigated to verify the accuracy of IS and to understand high FF from the PSCs-Fe₃O₄ W/H and the PSCs-Fe₃O₄ as well. Single charge carrier devices were fabricated and Mott-Gurney law was applied to estimate either electron mobility of PCBM or hole mobility of PTB7-F20. The details of single charge carrier devices fabrication and the method using Mott-Gurney law to estimate charge carrier mobilities are described in SI 8.

As shown in Fig. S8, hole mobilities (\(m_h\)) of 4.43 \(\times\) 10⁻⁴ cm²/Vs, 2.38 \(\times\) 10⁻⁴ cm²/Vs and 1.09 \(\times\) 10⁻⁴ cm²/Vs are observed from the PTB7-F20 incorporated with Fe₃O₄ MNPs and then followed with an external magnetostatic field alignment, the PTB7-F20 incorporated with Fe₃O₄ MNPs and pristine PTB7-F20, respectively. Electron mobilities (\(m_e\)) of 5.25 \(\times\) 10⁻⁴ cm²/Vs, 2.33 \(\times\) 10⁻⁴ cm²/Vs and 1.18 \(\times\) 10⁻⁴ cm²/Vs are observed from the PC₇₁BM incorporated with Fe₃O₄ MNPs and then followed with an external magnetostatic field alignment, the PC₇₁BM incorporated with Fe₃O₄ MNPs and pristine PC₇₁BM, respectively. Both enlarged hole mobil-

**Figure 6** | (A) Photocurrent density versus effective voltage (\(J_{ph} - V_{eq}\)) characteristics of PSCs under constant incident light intensity (AM 1.5 G, 100 mW/cm²), (B) photocurrent density (\(J_{sc}\)) versus the light intensity, and (C) open-circuit voltage (\(V_{oc}\)) versus of the light intensity. (The lines in (B) represent fits to the expression \(J_{sc} \propto I\) while the lines in (C) represent fits to the expression \(V_{oc} = S \ln(I/I_0)\), and (D) Device efficiencies (%) versus of BHJ film thickness (nm).

**Figure 7** | Nyquist plots at \(V = V_{oc}\) for PSCs under light irradiation.
ity of PTB7-F20 and electron mobility of PC71BM are observed from PTB7-F20 and PC71BM incorporated with Fe3O4 MNPs and then followed with an external magnetostatic field alignment, respectively. Consequently, reduced charge carrier recombination and enlarged JSC and FF are observed from the PSCs-Fe3O4 W/H. While the microscopic origin of enhanced mobility remains uncertain at this point, we speculate that aligned dipoles by an external magnetostatic field may facilitate charge carriers to escape shallow traps; thus, improving their mobilities17,38.

In conclusion, we have investigated the influence of magnetic nanoparticles and an external magnetostatic field on the PCEs of PSCs. The optimization of BHJ thin film morphology, suppression of charge carrier’s recombination and enhancement in free carrier collection result in more than 50% enhanced efficiency from the PSCs fabricated by BHJ composite blended with Fe3O4 magnetic nanoparticles and then followed with an external magnetostatic field alignment. Our work represents an evolution of PSCs that applications of magnetic nanoparticles and magnetostatic field alignment to BHJ composite have proven to be an extraordinarily effective way to enhance power conversion efficiency of PSCs.

Methods

Materials. PTB7-F20, PC61BM and PC71BM were provided by 1-Material Inc. (NREL). PBDTTT-C-T was provided by Prof. Y. F. Li and Prof. J. H. Hou in the Institute of Chemistry at the Chinese Academy Science, P. R. China. PT3HT was purchased from Rekje Metal Inc. All materials used as received without further purification. Fe3O4 MNPs toluene solution was purchased from Sigma-Aldrich. The size of Fe3O4 MNPs is ~5 nm.

Device Preparation. The PSCs architecture is ITO/PEDOT:PSS/BHJ active layer/ Calcium/Aluminum, where ITO is indium-doped tin oxide, PEDOT:PSS is poly(ethylenedioxythiophene):poly(styrenesulfonate), and the BHJ active layer is poly(3-hexylthiophene):PC61BM. ITO coated glass slides are firstly cleaned with detergent, followed by ultrasonic washing in deionized water, acetone, isopropanol, and subsequently dried in an oven overnight. The ITO is treated with oxygen plasma for 40 min to modify the surface. Then, PEDOT:PSS is coated on the ITO surface, followed by ultrasonic washing and dried in an oven at 80 °C for 10 min. The polymer:fullerene blend including PTB7-F20:PC71BM, PBDTTT-C-T:PC71BM and P3HT:PC71BM is then spin-coated from a binary solution of polymer and fullerene in chloroform, tetrahydrofuran, and toluene with a concentration of 10 mg/mL. After spin-coating, the active layer is annealed at 150 °C for 10 min in the dark. The BHJ active layer is then sequentially spin-coated on top of the PEDOT:PSS layer with a thickness of ~100 nm. For the control PSCs, the active layer was spin-coated from a binary solution of polymer and fullerene in o-DCB with a concentration of 10 mg/mL. For PSCs-Fe3O4 and PSCs-Fe3O4 W/H, the active layers were spin-coated from a ternary solution of polymer, fullerene and small amount of Fe3O4 MNPs (e.g. PTB7-F20:PC71BM BHJ composite (1:1.5, w/w, 10 mg/mL in o-DCB) mixed with Fe3O4 MNPs (1 mg/mL in toluene) by a volume ratio of 5%) (Fig. 2D). During the processing for PSCs-Fe3O4 W/H, an external magnetic field is applied to align the MNPs inside the active layer. The direction of magnetostatic field is perpendicular to the ITO substrate. The magnetostatic field is generated by square magnet (C750, 3/4’’ Cube, Licensed NdFeB, 40 Gauss, the distance to the ITO substrates is ~10 cm) (Fig. 2E). Its direction and intensity is manipulated by tuning the magnet pole direction (North and South) as well as adjusting the distance between these two square magnets, respectively. By using such specific magnet, the distance and intensity on the surface of active layer is controlled to ~10 cm and ~400 G, respectively. Finally, top electrode (Ca and Al) are sequentially deposited onto the active layer under a pressure of ca. 5 × 10−5 mbar (Fig. 2C).

Characterization and Measurement. The J–V curves characteristics are measured using a Keithley 2400 Source Measure Unit. The solar cells are characterized using a Newport Air Mass 1.5 Global (AM 1.5 G) full spectrum solar simulator with irradiation intensity of 100 mW/cm². The light intensity is measured by a silicon detector (with KG-5 visible color filter) which is calibrated by National Renewable Energy Laboratory (NREL). Device masks were made using laser beam cutting technology and had well-defined areas of 0.16 or 0.045 cm². GISAXS experiments were done at the Advanced Photon Source at Argonne National Laboratory. The IS spectra are recorded during the processing for PSCs-Fe3O4 W/H, an external magnetic field is applied to align the MNPs inside the active layer. The direction of magnetostatic field is perpendicular to the ITO substrate. The magnetostatic field is generated by square magnet (C750, 3/4’’ Cube, Licensed NdFeB, 40 Gauss, the distance to the ITO substrates is ~10 cm) (Fig. 2E). Its direction and intensity is manipulated by tuning the magnet pole direction (North and South) as well as adjusting the distance between these two square magnets, respectively. By using such specific magnet, the distance and intensity on the surface of active layer is controlled to ~10 cm and ~400 G, respectively. Finally, top electrode (Ca and Al) are sequentially deposited onto the active layer under a pressure of ca. 5 × 10−5 mbar (Fig. 2C).

Figure 8 | J^1/2 versus V–Vbi for (A) hole-only diode made by PTB7-F20 and (B) electron-only diodes made by PC71BM.
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Author contributions
K.W., C.Y., C.L., X.W.H. and C.H.H. conducted the experiments. S.C. involved deep discussion of the project and IS measurement. X.G. thought of the idea and supervised the project.

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