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Synthesis, Characterization and Performance of P3HT-Azide-PCBM Microgel

Guangmin Wei^{1, 2}, Xinxin Li², Di Jia², and He Cheng^{1, 3, *}

¹Dongguan Institute of Neutron Science (DINS), Dongguan 523808, China ²State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, CAS, Beijing 100190, China ³China Spallation Neutron Source (CSNS), Institute of High Energy Physics (IHEP), CAS, Dongguan 523803, China

Spherical Poly(3-hexylthiophene)-azide-[6,6]-phenyl-C₆₁-butyric acid methyl ester (P3HT-azide-PCBM) microgel was synthesized by introducing an azide cross-linkable group into the conjugated polymer. Its UV-vis spectrum shifts blue as a result of the systematic disruption of planarity along the P3HT backbone and a reduction in long range conjugation. And the corresponding fluorescence spectrum also indicates that a strong intra-molecular photo-induced electron transfer is originated from the covalent linkage of PCBM moiety to the P3HT backbone via the hexyl bridge upon photo-excitation. Combined Gel Permeation Chromatography (GPC), dynamic and static light scattering (DLS and SLS) measurements prove that the resultant P3HT-azide-PCBM copolymer is a uniform spherical microgel with a hydrodynamic radius of 130 nm at room temperature. The spherical P3HT-azide-PCBM microgel can be used as electron donor or compatibilizer in bulk-heterojunction (BHJ) devices, but its introduction reduces the photovoltaic performance compared with the blend of P3HT/PCBM, because the hole mobility in the crosslinked polythiophene backbones is largely decreased.

Keywords: P3HT-Azide-PCBM, Microgel, Bulk Heterojunction Solar Cells, Stability, Nano-Morphology.

1. INTRODUCTION

Polymer based organic photovoltaics have attracted lots of attentions as a potential candidate of costeffectiveness light-weighted flexible solar cells.^{1,2} A significant breakthrough has been achieved with the advent of bulk-heterojunction (BHJ) devices based on π -conjugated polymers as electron donors and fullerene derivatives as electron acceptors.^{3,4} Although a number of polymerfullerene combinations have been tested,^{5,6} BHJ solar cells based on poly(3-hexylthiophene) (P3HT) and the fullerene derivative [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) still represent the state of the art in organic photovoltaics with reproducible efficiencies as high as 5%.⁷

A key parameter for efficient BHJ solar cells is the three-dimensional nano-morphology of the active layer that provides a large interfacial area for exciton dissociation.⁸ Though the active layer of BHJ solar cells can be easily produced by spin casting of a blend solution on substrates, the control of donor–acceptor blend morphology is extremely difficult since the morphology is obtained by kinetically trapping of a non-equilibrium state during the process of crystallization coupled with spinodal decomposition. Most BHJ polymer solar cells are not thermally stable because subsequent exposure to heat will drive further development of the morphology toward a state of crystallization and macrophase separation in the micrometer scale.^{9, 10}

One major approach to improve the thermal stability of conjugated polymer-fullerene BHJ photovoltaic devices is the use of chemical cross-linkable units to prevent phase segregation in active layer. In 2005, Gaudiana et al. synthesized cross-linkable fullerene derivatives containing glycidyl functionality. They succeeded in suppressing the large aggregation of the fullerene derivative under thermal annealing after acid-catalyzed cross-linking.¹¹ In 2009, Hashimoto et al. prepared a cross-linkable regioregular poly(3-(5-hexenyl)thiophene)

^{*}Author to whom correspondence should be addressed.

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(P3HNT). P3HNT underwent cross-linking at the vinyl groups of the side chains upon a thermal treatment and the formation of large aggregations of PCBM was prevented in P3HNT:PCBM films even after prolonged thermal annealing.¹² In 2012, Kim et al. introduced azide cross-linkable units to P3HT and produced a solvent-resistant hole-transporting material for OTFTs and an *in-situ* compatibilizer in OPVs.¹³ Unfortunately, the chemical cross-linking will lead to significantly reduced device performance in spite of the stabilized P3HT/PCBM morphology.^{11, 12} Therefore, the development of materials with both stable morphology and high performance remains a challenge, though the cross-linking concept is simple and powerful.

In the previous studies, in-situ chemical cross-linking in BHJ films right after the formation of the optimal morphology is the typical strategy, because it is supposed to keep the pre-formed suitable structure while improving morphological stability.^{11, 14, 15} However, the decrease of the contrast during chemical reaction and possible reaction induced phase separation result in an elusive morphology in the active layer. Therefore, compared with the insoluble and inmeltable photo-crosslinked active layer, it is more desirable to prepare the conducting polymerfullerene copolymer to adjust the morphology directly. In this paper, the synthesis, characterization, optical and photovoltaic properties of a cross-linkable P3HT-azide-PCBM copolymer microgel are reported. In order to gain a deeper insight into the structure of the P3HT-azide-PCBM, dynamic and static light scattering are used. Although there are many choices for the reactive function, we adopt an azide group at the end of the side chain as the crosslinkable site because this kind of cross-linkable unit is easy to prepare and highly reactive.

2. EXPERIMENTAL DETAILS

2.1. Characterization

¹HNMR spectra were recorded at 298 K with a Bruker Avance 400 NMR spectrometer. Number average (M_n) and weight average (M_w) molecular weights were determined by GPC with polystyrene as standard and CHCl₃ as eluent. FTIR spectra were obtained with Bruker EQUINOX55 FTIR spectrometer. Fluorescence spectra were performed on a Cary Eclipse spectrometer. The viscosity of o-DCB was measured by Ubbelohde viscometers (capillary diameter is 0.2 ± 0.01 mm). Light scattering experiments were carried out on a modified LS spectrometer equipped with a multi- τ digital time correlator (ALV5000).¹⁶ The electrochemical cyclic voltammetry experiments were conducted on a CHI650D Electrochemical Workstation with glassy carbon disk, Pt wire, and an Ag/Ag⁺ electrode as the working electrode, counter electrode, and reference electrode, respectively in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution.

2.2. Materials

3-hexylthiophene was purchased from Puyang Huicheng Electronic Material Co., Ltd. 3-bromothiophene, *N*-bromosuccinimide (NBS), *n*-butyllithium (*n*-BuLi, 1.6 M solution in hexanes), 1,6-dibromohexane, 1,3-dibromo-5,5-dimethylhydantoin, Lithium diisopropylamide (LDA, 2.0 M solution in THF), anhydrous ZnCl₂, Ni(dppp)Cl₂ and 18-crown-6 were purchased from J&K Scientific Ltd. NaN₃ was purchased from Xiya Reagent. PCBM was purchased from Solarmer Energy, Inc. All of these chemicals were used as received. THF and *n*-hexane were dried over Na/benzophenone. DMF was dried by anhydrous MgSO₄.

2.3. Synthesis of Monomers

2.3.1. Synthesis of 2-Bromo-3-Hexylthiophene (2)

3-hexylthiophene (1) (5.00 g, 29.7 mmol) was dissolved in dry THF (50 mL) under an argon atmosphere. NBS (5.81 g, 32.7 mmol) was separated into 5 parts, and each part was added every 5 min at 0 °C. After adding the last part of NBS, the solution was stirred at 0 °C for 10 min. Then the solution was stirred at room temperature for 2 hrs. The solvent was removed in vacuum and 100 mL of hexane was added (to precipitate all the succinimide). The mixture was filtered and the solvent was removed in vacuum. The title compound was purified by the column chromatography (silica/hexane).^{17, 18}

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2.3.2. Synthesis of 3-(6-Bromohexyl)Thiophene (4)

3-bromothiophene (3) (10.20 g, 62.6 mmol) was dissolved in dry hexanes (100 mL) under an argon atmosphere, and cooled to -78 °C. n-BuLi (40 mL, 62.6 mmol) was added dropwise to the stirred solution, after which the solution was stirred at -78 °C for 10 min. Then, dry THF was added dropwise via a syringe (ca. 10-15 mL) until white 3-lithiothiophene salt precipitated. The solution was then stirred at -78 °C for 1 hr, and allowed to warm to -10 °C. Dry THF (10 mL) and 1,6-dibromohexane (40 mL, 260.0 mmol) were added to the solution, after which the solution was stirred at -10 °C for 10 min and then warmed to room temperature. After stirred at room temperature for 2 hrs, the solution was diluted with dry hexane (100 mL). The separated organic layer was washed with water, dried over anhydrous MgSO₄, and concentrated in vacuum. Excess remained 1,6-dibromohexane in crude product was removed by vacuum distillation, and then the product was purified by column chromatography using hexane as the eluent.^{13, 14}

2.3.3. Synthesis of 2-Bromo-3-(6-Bromohexyl) Thiophene (5)

3-(6-bromohexyl)thiophene (4) (4.33 g, 17.5 mmol) was dissolved in dry THF (60 mL). The solution was cooled in an ice bath, and 1,3-dibromo-5,5-dimethylhydantoin (2.63 g, 9.2 mmol) was added and the solution was stirred at room temperature for 2 hrs. After concentrating

the solution in vacuum, dry hexane was added, and the solution was filtered and concentrated in vacuum again. Further purification was carried out via silica gel column chromatography, using hexane as the eluent.¹⁴

2.4. Synthesis of Polymers 2.4.1. Synthesis of P3HT-Br (6)

LDA (15 mL, 30.0 mmol) was added dropwise to the mixture of 2-bromo-3-(6-bromohexyl)thiophene (5) (1.96 g, 6.0 mmol) and 2-bromo-3-hexylthiophene (2) (6.68 g, 27.0 mmol) in dry THF (80 mL) at -78 °C. After 1 hr reaction at -78 °C, anhydrous ZnCl₂ (5.11 g, 37.5 mmol)/dry THF (50 mL) solution was added dropwise via a syringe. The solution was stirred at -78 °C for 30 min and then warmed slowly to room temperature. Polymerization initiated by adding Ni(dppp)Cl₂ (81.3 mg, 0.15 mmol) to the solution and the reaction was carried out at room temperature for overnight. The polymerization was ended by 5 mL 1.0 M aqueous HCl. The polymer was precipitated with methanol (450 mL) containing 7 M NH₃ (6 mL) to neutralize it, and the resulting precipitate was then filtered. Oligomers and impurities in the product were removed by soxhlet extractions with methanol and hexane, followed by chloroform extraction. The resulting solid was dried under vacuum to yield the product (6).¹³

2.4.2. Synthesis of P3HT-Azide (7) Delivered by Ingentation P3HT-Br (6) (500 mg) was dissolved in THF (125 mL). The NaN₃ (150 mg, 2.28 mmol) and 18-crown-6 (600 mg, 2.28 mmol) was dissolved in DMF (40 mL) and sonication was applied to obtain homogeneous solution. DMF solution was added to THF solution and then refluxed for overnight under an argon atmosphere. The polymer was precipitated with methanol and the resulting precipitate was then filtered. Residual NaN₃ was removed by soxhlet extractions with methanol for overnight. The resulting solid was dried under vacuum to yield the product (7).¹³

2.4.3. Synthesis of P3HT-Azide-PCBM (8)

P3HT-azide (500 mg) and PCBM (250 mg) were dissolved in *o*-DCB (15 mL), and the solution was stirred at 150 °C for overnight. The solution was cooled to room temperature and filtered with 0.45 μ m Millex Millipore PTFE membrane. The polymer was precipitated with methanol and the resulting precipitate was then filtered. Residual PCBM was removed by soxhlet extractions with methanol for overnight. The resulting solid was dried under vacuum to yield the product (**8**).

2.5. Device Fabrication and Characterization

Indium-tin oxide (ITO) coated glass substrates were subjected to ultrasonication in different solvent systems including acetone, 2% soap in water, deionized water, and then isopropanol. Three different solutions

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P3HT/PCBM (1:1, weight ratio), P3HT-azideof PCBM/PCBM (1:0.8, weight ratio) and P3HT/P3HTazide-PCBM/PCBM (1:0.2:1.12, weight ratio) in o-DCB $(10 \text{ mg mL}^{-1}, \text{ based on the polymer weight concentration})$ were prepared and stirred at 110 °C for more than 24 hrs. After spin-coating a 30 nm layer of poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) onto a pre-cleaned ITO coated glass substrates, the solution was spin-coated. The devices were completed by evaporating Ca/Al metal electrodes with area of 0.04 cm² defined by masks. The current-voltage curves are measured under 100 mW cm⁻² standard AM 1.5 G spectrum using a XES-70S1 (SAN-EI ELECTRIC CO., LTD.) solar simulator (AAA grade, 70 mm × 70 mm photo-beam size). 2×2 cm Monocrystalline silicon reference cell (SRC-1000-TC-OZ) was purchased from VLSI Standards Inc. The mismatch between solar simulator and the standard solar spectrum has been considered. The average PCE were obtained from more than 30 pieces of devices.¹⁹

3. RESULTS AND DISCUSSION 3.1. Synthesis of the Microgel

Scheme 1 depicts the synthetic approach to obtain P3HTazide-PCBM. Cycloaddition of the azide unit to PCBM completes the synthesis.^{20, 21} The azido route for the attachment of PCBM, rather than atom transfer radical addition (ATRA) is used as it is simple and versatile.^{22, 23} ¹HNMR integration of the proton at the 4-position of the thienyl ring shows that the HT regioregularity of P3HT-Br is ~98% with respect to the α -methylene protons (2H at 2.78 ppm). The molar ratio of 3-(azidohexyl)thiophene monomer in P3HT-azide copolymer, *x*, can be estimated from the integral area ratio of the peaks for $-CH_2N_3$ ($\delta =$ 0.92 ppm) and $-CH_3$ ($\delta =$ 3.28 ppm) groups. According to the following equation,

$$\frac{3(1-x)}{2x} = \frac{A_{-\rm CH_3,\,\delta=0.92\ ppm}}{A_{-\rm CH_2N_3,\,\delta=3.28\ ppm}} = \frac{3.145}{0.252} \tag{1}$$

x can be calculated as 0.11. GPC analysis indicates that the number average (M_n) and weight average (M_w) molecular weights, and polydispersity index (PDI) of P3HT-azide copolymer are 5800 g/mol, 7400 g/mol and 1.26, respectively. Based on the molar ratio of 3-(azidohexyl)thiophene monomer in P3HT-azide copolymer (x) and the number average molecular weights (M_n) , a degree of polymerization (DP) for P3HT-azide copolymer can be estimated. The result shows that each P3HT-azide copolymer chain contains three 3-(azidohexyl)thiophene monomers and 31 3-hexylthiophene monomers on average.

In Scheme 1, the bromine groups of P3HT-Br are replaced with azide units (N_3) by NaN₃ and 18-crown-6 as a phase transfer catalyst in THF/DMF mixture. Then the azide units of P3HT-azide have an addition reaction with PCBM in *o*-DCB solution. The formation of the azide and

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Scheme 1. Synthetic route for P3HT-azide-PCBM.

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its subsequent functionalization with PCBM can be monitored by IR spectroscopy.^{15, 24} As shown in Figure 1, after azidation, a strong characteristic band for the azide group at 2090 cm⁻¹ (Fig. 1(b)) is observed in FTIR spectrum. After cycloaddition to PCBM, the peak at 2090 cm⁻¹ completely disappears (Fig. 1(c)). The appearance and disappearance of the sharp peak of the azide unit at 2090 cm⁻¹, conform that azidation and cycloaddition reactions are successful.

To get a deeper insight into the possible changes in molecular packing of polymers due to azide unit introduction and cycloaddition, UV-vis spectrum is measured in Figure 2. The absorption peak at 460 nm is the extensive $\pi - \pi^*$ transition due to the conjugated P3HT unit,²³ and the absorption peak at 330 nm is from the PCBM moiety.^{22, 25} When P3HT and PCBM are physically mixed, the corresponding UV-vis spectrum of the blend has two distinct absorption peaks at 463 nm and 330 nm, respectively. However, after the introduction and cycloaddition of azide unit to PCBM, the absorption peak of P3HT-azide-PCBM has an obvious blue shift as a result of the systematic disruption of planarity along the backbone and a reduction in long range conjugation. This can be further proved by fluorescence measurement.



Figure 1. FTIR spectrum of P3HT-Br (a), P3HT-azide (b), and P3HT-azide-PCBM (c). The dash line is used to guide the eye.



Figure 2. UV-vis spectra of P3HT (a), P3HT/PCBM blend (b) and P3HT-azide-PCBM (c) in *o*-DCB at room temperature.

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It is well known that the fluorescence is useful for probing the intramolecular charge transfer dynamics between donor and acceptor.²⁶ Figure 3 illustrates the fluorescence spectrum of P3HT-azide-PCBM in o-DCB in comparison with those of pure P3HT and P3HT/PCBM blend. To make a quantitative comparison, a P3HT/PCBM (1:0.5, weight ratio) blend solution is prepared to ensure that the molar ratio of PCBM in the blend is similar (11%) to that in P3HT-azide-PCBM. Because of the intermolecular photo-induced electron transfer, the blend has only $\sim 8.2\%$ quenching of the fluorescence of pure P3HT (Figs. 3(a) and (b)). While P3HT-azide-PCBM has ~58.8% quenching according to the integral of the fluorescence band (see Figs. 3(a) and (c)). These results clearly prove that a strong intramolecular photoinduced electron transfer originating from the covalent linkage of PCBM moiety to the P3HT backbone via the hexyl bridge in P3HT-azide-PCBM. The intra-molecular hybrid structure of P3HTazide-PCBM enables closer contact of the PCBM moiety with the thienyl ring via the hexyl bridge, and facilitates their π - π interactions. However, in P3HT/PCBM blend counterpart, the π - π interactions between P3HT and PCBM can only take place intermolecularly, resulting in a weaker quenching.

3.2. Characterization of the Solution Structure

To investigate the solution structure of P3HT–azide-PCBM copolymer, Light scattering experiments are carried out.

In dynamic light scattering (DLS), they hydrodynamical radius $R_{\rm h}$ can be determined from the Stokes-Einstein relation $R_{\rm h} = k_{\rm B}T/6\pi\eta D$, where η is the solvent viscosity.²⁵ Because the viscosity will change with temperature,²⁷ the temperature dependence of viscosity are measured first. As shown in Figure 4, the relation between viscosity and temperature of *o*-DCB can be represented by the equation:

$$n = 0.1847 + 0.8390e^{-(t-21.19)/59.49}$$
(2)

Figure 5(a) is the temperature evolution of intensityintensity time correlation function of P3HT-azide-PCBM in *o*-DCB. There is a slight decrease of the characteristic



Figure 3. Fluorescence spectra of P3HT (a), P3HT-azide-PCBM (b), and P3HT/PCBM blend (c) in o-DCB at room temperature. The excitation wavelength was 450 nm.

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Figure 4. The temperature dependence viscosity of the o-DCB.

decay time, τ , as temperature increases, and the hydrodynamic radius $R_{\rm h}$ has a little decrease correspondingly. Figure 5(b) shows the hydrodynamic radius of P3HTazide-PCBM in o-DCB is about 130 nm at 20 °C and decreases slightly with temperature. It implies that it is not a copolymer chain, but a microgel of P3HT-azide-PCBM in o-DCB solution. From GPC measurement, the number average molecular weight (M_n) of P3HT-azide copolymer is about 5.8 kg/mol. If each PCBM reacts with only one azide unit in cycloaddition, the number average molecular weight of P3HT-azide-PCBM should be about 8.5 kg/mol, when each P3HT-azide copolymer chain contains three 3-(azidohexyl)thiophene monomers on average. However, the hydrodynamic radius of P3HT-azide-PCBM in o-DCB is about 130 nm at 20 °C, which is too large for a polymer chain with 8.5 kg/mol molecular weight.

The basic shape of P3HT-azide-PCBM in o-DCB can be determined from the ratio between its radius of gyration and hydrodynamic radius, R_g/R_h . This is because they are defined from different ways: R_g is related to the square average of the segmental distribution $\langle r_{ij}^2 \rangle$ and reflects the density distribution in real space, while R_h is related to the inverse segmental distribution $\langle |r_{ij}|^{-1}R_g \rangle$ and is equivalent to the radius of a hard sphere with the same translational diffusion coefficient.²⁸ Theoretically, for a coiled chain in a good solvent, $R_g/R_h = 1.5$, and for a uniform none draining sphere $R_{\rm g}/R_{\rm h}^{-} = 0.78^{.29}$ Figure 6 is the temperature evolution of $R_{\rm h}$, $R_{\rm g}$, $R_{\rm g}/R_{\rm h}$ of P3HT-azide-PCBM in o-DCB solution. The results indicate that the R_{g}/R_{h} of the P3HT-azide-PCBM particles keeps a constant of \sim 0.80 at different temperatures. Therefore, it is reasonable to conclude that the shape of P3HT-azide-PCBM microgel in o-DCB solution is close to a uniform sphere where PCBM acts as crosslinker.

It is known that *o*-DCB is a good solvent for both P3HT and PCBM, if P3HT-azide-PCBM formed in cycloaddition is a copolymer chain, the chain conformation should be a random coil with $R_g/R_h \sim 1.5$. However, the hydrodynamic radius of P3HT-azide-PCBM in *o*-DCB is about 130 nm which is too large for a random coil, and its $R_g/R_h \sim 0.8$. Therefore, we consider that the structure of P3HT-azide-PCBM formed in cycloaddition is a spherical microgel, which consists of solvent-penetrated crosslinked threedimensional polymer networks with dimensions between



Figure 5. The intensity-intensity time correlation functions (a) and the corresponding hydrodynamic radius (b) of P3HT-azide-PCBM in *o*-DCB at different temperatures.

50 nm to a few micrometers,³⁰ as illustrated in Figure 7. According to the literature, PCBM is an electron-acceptor and contains pentagonal and hexagonal rings.¹⁵ Thus, the reaction of azide with PCBM may proceed through mono, tri, even higher addition.³¹ The multi-addition leads to cross-linking microgel, where PCBM is just like a chemical cross-linker.

3.3. Photovoltaic Properties

The photovoltaic properties of the devices fabricated under optimal conditions are listed in Table I. For the BHJ OPV devices based on P3HT-azide-PCBM:PCBM and P3HT:P3HT-azide-PCBM:PCBM, the donor/acceptor (D/A) weight ratio of 1:0.8 and 1:0.2:1.12 are used in the active layer. As a vreference, the donor/acceptor (D/A) weight ratio for the device of P3HT:PCBM should be 1:1. Compared to the reference, the $V_{\rm oc}$ is slightly reduced when P3HT-azide-PCBM is used in the OPV devices. For the device of P3HT-azide-PCBM:PCBM, P3HT-azide-PCBM is used as the donor, and the J_{sc} and FF reduce greatly. While, for the device of P3HT:P3HT-azide-PCBM:PCBM, P3HT-azide-PCBM is used as the compatibilizer, and the J_{sc} and FF reduce slightly. The decrease of $J_{\rm sc}$ and FF may be attributed to the decrease in mobility with the presence of crosslinked P3HT-azide-PCBM microgel.

Thermal annealing of P3HT:PCBM composite provides external energy, which drives the P3HT to reorganize and



Figure 6. $R_{\rm h}$, $R_{\rm g}$, $R_{\rm g}/R_{\rm h}$ of P3HT-azide-PCBM in *o*-DCB at different temperatures.

self assemble. Through this morphological evolution, the featureless and homogeneous blend gradually reaches a bicontinuous interpenetrating D-A network with optimal D-A domain size.⁷ As a result, maximum interfacial area for efficient charge generation and a higher degree of nanoscale P3HT crystallinity can be achieved for better charge transport.³² Unfortunately, this optimal morphology is a kinetically trapped metastable state that readily moves toward a more thermodynamically stable state if thermal annealing at elevated temperature is applied constantly.^{10, 33, 34} The P3HT domain continues to undergo further crystallization, while the spherical PCBM, with its high molecular mobility, tends to diffuse out of the polymer matrix and aggregates into larger clusters or single crystals.³⁵ Considering that a photovoltaic device must be exposed to long-term sunlight irradiation, the accumulated heat may raise the operational temperature above the glass transition temperature (T_g) of polymers, thus destroying the optimal morphology, and deteriorating the device performance.³⁶ In order to enhance the thermal stability of the active layer, preserving the morphology by chemical cross linking of donor and acceptor is an ideal method,^{12, 37} but the introduction of cross-linking bridges in conjugated polymers often disturbs their molecular packing, significantly reducing their performance.¹¹ According to the previous studies, in the poly(3-alkylthiophene)s films, the π - π stacking of the polymers is largely affected by the packing of the side chains.^{38, 39} The introduction of large functionalities to the side chains can result in the decrease of crystallinity, thereby decreasing the hole mobility in the polythiophene chains.⁴⁰ Furthermore,



Figure 7. Schematic representation of the two different routes in cycloaddition.

Table I. Photovoltaic performance of the device based on P3HTazide-PCBM:PCBM, P3HT:P3HT-azide-PCBM:PCBM and P3HT:PCBM under the illumination of AM 1.5G, 100 mW/cm².

Samples	$V_{ m oc}$ (V)	$J_{\rm sc}$ (mA/cm ²)	FF (%)	PCE (%)
P3HT-azide-PCBM:PCBM	0.627	1.41	30.7	0.272
P3HT:P3HT-azide-PCBM:PCBM	0.626	5.26	64.6	2.11
P3HT:PCBM	0.635	5.73	69.7	2.53

P3HT-azide-PCBM is a chemical cross-linked spherical microgel, and its chain mobility is largely reduced in the active layer.

4. CONCLUSIONS

In summary, the synthesis, characterization, optical and photovoltaic properties of a cross-linkable P3HT-azide-PCBM microgel are reported. P3HT-azide-PCBM is synthesized by introducing an azide cross-linkable group into the conjugated polymer. Compared with P3HT/PCBM blend, the absorption band of P3HT-azide-PCBM shifts blue greatly and its fluorescence intensity is deeply quenched. According to DLS measurement, in *o*-DCB solution, the P3HT-azide-PCBM copolymer is not a polymer chain, but a chemical cross-linked spherical microgel. The spherical shape of P3HT-azide-PCBM has large influence on its photovoltaic performance because the hole mobility in the polythiophene chains is reduced.

Notes

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The authors declare no competing financial interest.

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