

Development of Click Chemistry in Polymerization and Applications of Click Polymer

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Abstract: Click chemistry had enjoyed a wealthy decade after it was introduced by K.B.Sharpless and his co-worker on 2001. Since there is no optimized method for synthesis of click polymer, therefore, this paper introduced three click reaction methods such as catalyst, non-catalyst and azide-end capping for fluorene-based functional click polymers. The obtained polymers have reasonable molecular weight with narrow PDI. The polymers are thermally stable and almost emitted blue light emission. The synthesized fluorene-based functional click polymers were characterized to compare the effect of click reaction methods on polymer electro-optical properties as well as device performance on quasi-solid-state dye sensitized solar cells (DSSCs) applications. The DSSCs with configuration of SnO₂:F/TiO₂/N719 dye/quasi-solid-state electrolyte/Pt devices were fabricated using these click polymers as a solid-state electrolyte components. Among the devices, the catalyzed click polymer composed device exhibited a high power conversion efficiency of 4.62% under AM 1.5G illumination (100 mW/cm²). These click polymers are promising materials in device application and Cu^I-catalyst 1, 3-dipolar cycloaddition click reaction is an efficient synthetic methodology.

1. Introduction

Click chemistry¹ had enjoyed a healthy decade. The advantages of this reaction are high fidelity, quantitative yields, applicability under mild reaction conditions, oxygen and water tolerance, simple work-up of products, and it is highly chemoselective in the formation of the desired 1, 4-disubstituted 1, 2, 3-triazole even in presence of a large variety of functional groups. This methodology has been ap-

plied widely in organic chemistry,² supramolecular chemistry,³ drug discovery,⁴ bioconjugations,⁵ and materials science.⁶ Since the initial discovery of Cu^I-catalyzed alkyne-azide coupling, numerous successful examples has been recorded earlier, but as of yet, no systematic study of optimal conditions has been reported for both catalyst⁷⁻⁹ and non-catalyst systems.¹⁰⁻¹¹ To further understanding of the azide-alkyne click reaction, it is necessary to optimize the conditions under which the reaction was conducted to achieve high rates and yields with minimal synthetic manipulation. The primary drawbacks of the polymers synthesized by click chemistry are long reaction time, poor product solubility,⁷⁻⁸ and no opti-



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mized method. However, the synthesis of conjugated polymers by 1, 3-dipolar cycloadditions has been conspicuously absent and only few examples have been reported.⁷⁻⁹

There are many methods employed in 1, 3-dipolar cycloaddition click reactions. The renowned methods are (1) copper catalyst with polytriazoles⁷ or triethylamine(TEA)^{9,12} as copper(I)-stabilizing ligands, (2) copper catalyst without ligand,⁸ and (3) non-catalyst (using polar solvent with moderated temperature).¹⁰

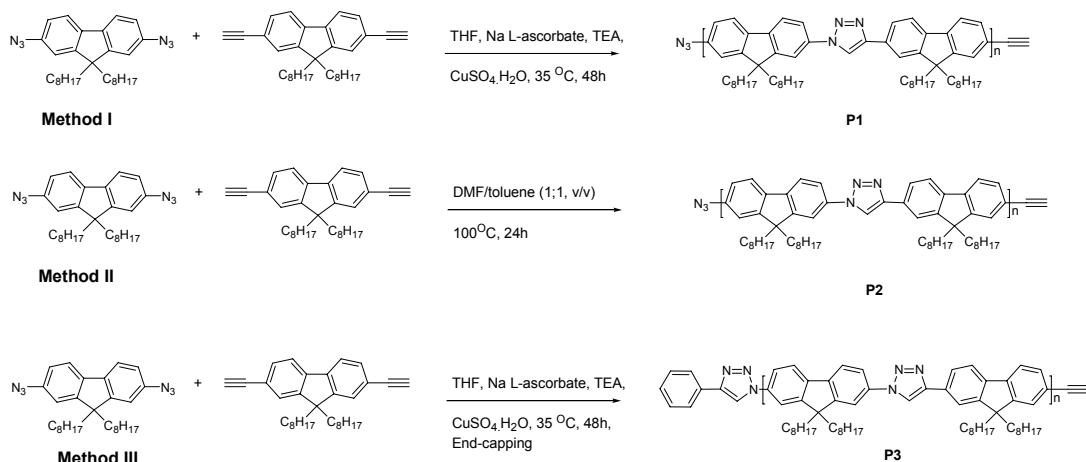
Among the reaction conditions of click chemistry, perhaps Cu^I-catalyst 1, 3-dipolar cycloaddition is a choice of reaction for chemist. But it is very difficult to remove the metal completely from resulting polymers.

The catalyst residues can be detrimental to the electronic and optical properties of polymers such as light emissions from conjugated polymers can be quenched by metallic traps.¹⁰ On the other hand 1,3-dipolar cycloaddition reaction involving azides and alkynes for the preparation of conjugated polymer and meanwhile showed the necessity of controlling the polymerization conditions because of the high reactivity of the azide and alkyne functionalities. One possibility to gain control and inhibit auto-polymerization of the monomers is to put the functional groups in two separate monomers.¹³ To control auto-polymerization, it may be necessary to end-cap in click polymerization.

In this article, three click polymers catalyzed (P1), non-catalyzed (P2) and azide-end capping (P3) were synthesized. These click polymers are characterized and compared their electro-optical properties as well as device performances on quasi-solid-state dye-sensitized solar cells. The device was fabricated with the configuration of SnO₂:F/TiO₂/N719Dye/quasi-solid-state electrolyte/Pt.

2. Materials and Methods

All reagents used were purchased from Sigma-Aldrich Co. and used without further purification. The solvents were purified using normal procedures and were handled in a moisture free atmosphere. Column chromatography was carried out using silica gel (Merck, 250-430 mesh). Conventional Schlenk techniques were used and the reactions were carried out under a N₂ atmosphere unless otherwise noted. The ¹H-NMR spectra were recorded on a Bruker AM-300 spectrometer and the chemical shifts were recorded in ppm units with chloroform as an internal standard. The absorption and PL spectra were measured by using a Shimadzu UV-3100 UV-visible spectrometer and Hitachi F-4500 fluorescence spectrophotometer, respectively. The solid-state emission measurements were carried out by supporting each film on a quartz substrate that was mounted to receive front-face excitation at an angle < 45°. Each polymer film was excited with several portions of the visible spectrum from a xenon lamp. The molecular weight and polydispersity index of the polymer were determined by gel permeation chromatography (GPC) using Plgel 5 μm MIXED-C column on an Agilent 1100 series liquid chromatography system with THF as an eluent and calibration with polystyrene standards. Thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851, DSC 822 analyzer under an N₂ atmosphere at a heating rate of 10 °C/min. Cyclic voltammetry (CV) was carried out using a Bioanalytical Systems CV-50W voltammetric analyzer at a potential scan rate of 50-100 mV/s in a 0.1 M solution of tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) in anhydrous acetonitrile. Each polymer film was coated on a Pt disc electrode (0.2 cm²) by dipping the electrode into a solution of the polymer (10 mg/mL). A platinum wire and an Ag/AgNO₃ electrode were used as the



Scheme 1. Synthesis of Click polymers (P1-P3).

counter and reference electrodes, respectively. All the electrochemical experiments were carried out in a glove box under an Ar atmosphere at room temperature.

2.1 Procedures for the synthesis of polymers

2, 7-Diazido-9, 9-dioctyl-fluorene,¹⁴ and 2, 7-diethynyl-9, 9-dioctylfluorene,¹⁵ were synthesized using a slight modification of the method reported in the literature.

2.2 Method (I) for the synthesis of polymers, P1

Diazide- and diethynyl-based monomers (1:1 equiv.) and sodium L-ascorbate (10 mol %) were dissolved in THF (2-3 mL) under N₂ flow in a flame dried Schlenk flask and added triethylamine (TEA) (0.2-0.3 mL) as a ligand to the mixture.^{9,12} The flask was flushed with N₂ for 20-30 min. The mixture was frozen and evacuated three times, which was followed by the addition of CuSO₄·5H₂O (5 mol %) under a flow of N₂ gas. The mixture was stirred at 30-35 °C for 48 h. After completion of click polymerization, the THF was removed under vacuum and the mixture was dissolved in chloroform, washed with an aqueous NH₄OH solution followed by water. The organic layer was separated and the solvent was

removed. The resulting polymer was precipitated into methanol. In the above procedure, the reaction will not proceed if TEA is not added, even after 10 days at room temperature. By adding TEA and increasing the reaction temperature, reasonable molecular weight polymers could be synthesized by click chemistry. A recent systematic investigation conducted in organic media revealed that aliphatic amine ligands consistently led to significantly faster rates as compared to other amines. This could be due to a number of factors, including electron back donation from the copper center to the alkyne, and the stronger basicity and enhanced ability of aliphatic amine ligands relative to pyridine-based ligands.¹⁶

2.3 Polymer 1 (P1)

Yellow solid. ¹H-NMR (CDCl₃ 500 MHz): δ (ppm) 8.39 (s), 8.35 (s), 8.03 (s), 7.95-7.91 (m), 7.86-7.79 (m), 7.78-7.73 (m), 7.09-7.07 (m), 7.03 (d), 2.19-2.10 (m), 2.05-1.99 (m), 1.27-1.10 (m), 0.95-0.78 (m), 0.72-0.66 (m). Anal Calcd for (C₆₂H₈₂N₆)_n: C, 81.71; H, 9.06, N, 9.22. Found: C, 80.18; H, 9.29; N, 9.26.

2.4 Method (II) for the synthesis of polymers, P2

In a flame dried Schlenk flask were placed

Diazide- and diethynyl-based monomers (1:1 equiv.) and injected mixture of DMF/toluene (1:1 by volume). The reaction mixture was stirred under N₂ gas at 100 °C for one day. After that the reaction mixture was dilute with chloroform and added dropwise of a 10:1 mixture of hexane and chloroform through a cotton filter under stirring. The precipitates were allowed to stand overnight, collected by filtration, and dried under vacuum at room temperature to a constant weight.¹⁰ As no transition-metal catalyst is used in the process; this polymerization enjoys such advantages as being less toxic, environmentally friendlier, and economically sounder. This helps simplify the reaction procedures and enhance the polymerization efficiency.

2.5 Polymer P2

Yellow solid. ¹H-NMR (CDCl₃, 300 MHz): δ (ppm) 8.35 (s), 7.98-7.94 (m), 7.89-7.84 (m), 7.76-7.74 (m), 7.66-7.58 (m), 7.48-7.43(m), 7.32(s), 7.02(s), 2.18(m), 2.01-1.82 (m), 1.25-1.08 (m), 0.81 (m), 0.66 (m). Anal Calcd for (C₆₂ H₈₂ N₆)_n: C, 81.71; H, 9.06, N, 9.22. Found: C, 80.18; H, 9.29; N, 9.26.

2.6 Method (III) for the synthesis of polymers, P3

Diazide- and diethynyl-based monomers (1:1 equiv.) and sodium L-ascorbate (10 mol%) were dissolved in THF (2-3 mL) under flow of N₂ into a flame dried Schlenk flask and added to the mixture of triethylamine (2-3 mL) as a ligand.^{9,12} The flask was flushed with flow of N₂ for 20-30 min and the mixture was frozen and evacuated for three times and CuSO₄·5H₂O (5 mol%) was added under flow of N₂ gas. The mixture was allowed to stir at 30-35 °C for 48 hr. A little amount of phenylacetylene was used as an azide end-capping material after checking the precipitation of that reaction mixture and stirring for more few minutes. This study demonstrated the potential of 1, 3-dipolar cycloaddition reaction involving azides and alkynes for the preparation of

conjugated polymer and meanwhile showed the necessity of controlling the polymerization conditions because of the high reactivity of the azide and alkyne functionalities. One possibility to gain control and inhibit auto-polymerization of the monomers is to put the functional groups in two separate monomers.¹³ Therefore, to control the auto-polymerization azide was end-capped by phenylacetylene. The THF was removed under vacuum and the mixture was dissolved in chloroform, washed with aqueous NH₄OH solution and then water. The organic layer was separated and the solvent removed. The resulting polymer was precipitated into the methanol.

2.7 Polymer P3

Yellow solid. ¹H-NMR (CDCl₃, 300 MHz): δ (ppm) 8.36 (s), 8.34 (s), 8.01 (s), 7.97-7.90 (m), 7.84-7.79 (m), 7.69-7.66 (m), 7.51-7.50 (m), 7.49 (s), 3.16(s), 2.17-2.16 (m), 2.05-1.99 (m), 1.26-1.11 (m), 0.80-0.77 (m), 0.08 (m). Anal Calcd for (C₆₂ H₈₂ N₆)_n: C, 82.96; H, 8.75, N, 8.29. Found: C, 81.41; H, 8.97; N, 8.33.

2.8 Fabrication and measurement of DSSCs

The quasi-solid-state electrolyte consisted of I₂ (1.15 M), tetrabutylammonium iodide (TBAI) (2.4 M), and 1-propyl-3- methylimidazolium iodide (PMII) (3.95 M) in a co solvent of ethylene carbonate (EC) and propylene carbonate (PC) (0.4 mL, EC/PC=3/1 as weight ratio) with P1-P3 (50 mg) in an acetonitrile solution (0.2 mL). The DSSCs were fabricated using N719 dye (Ru[LL'(NCS)₂], L = 2,2'-bipyridyl-4,4'- dicarboxylic acid, L' = 2,2'-bipyridyl- 4,4'-ditetrabutylammonium carboxylate) as the photosensitizer and sandwiched between a TiO₂ thin film and a Pt counter electrode as the two electrodes. The DSSC was fabricated using the following process; a volume of ca. 10 μl/cm² of the transparent pastes (Ti-Nanoxide HT) was spread on FTO glass using the doctor blade method. The FTO

glass spread TiO₂ nanoparticles were heated to ca. 100 °C for approximately 30 min and ca. 450 °C for approximately 30 min. The TiO₂ deposited electrode was then cooled from 100 °C to 60 °C at a controlled cooling rate (3 °C/min) to avoid cracking of the glass. A Pt counter electrode was fabricated by spreading on FTO glass using the doctor blade method. The FTO glass spread Pt catalyst T/SP was heated to approximately 100 °C for 10 min before firing at 400 °C for 30 min. The N719 dye photosensitizer was dissolved in absolute ethanol to a concentration of 20 mg per 100 mL of solution. The nanoporous TiO₂ film was dipped in this solution at room temperature for 24 h. The dye-sensitized TiO₂ electrode was then rinsed with absolute ethanol and dried in air. The solid-state electrolyte was cast onto the N719 dye impregnated TiO₂, and dried at 60 °C for 2 h. The effective area of the DSSCs was 25 mm². The performance of photovoltaic devices were measured using a calibrated AM 1.5G solar simulator (Orel 300 W simulator, models 81150) with a light intensity of 100 Mw/cm² adjusted using a standard PV reference cell (2 cm x 2 cm monocrystalline silicon solar cell, calibrated at NREL, Colorado, USA) and a computer-controlled Keithley 236 source measure unit.

The PCE (η) of a solar cell given by

$$\eta = P_{\text{out}} / P_{\text{in}} = (J_{\text{sc}} \times V_{\text{oc}}) \times \text{FF} / P_{\text{in}}$$

$$\text{with FF} = P_{\text{max}} / (J_{\text{sc}} \times V_{\text{oc}})$$

$$= (J_{\text{max}} \times V_{\text{max}}) / (J_{\text{sc}} \times V_{\text{oc}})$$

where P_{out} is the output electrical power of the device under illumination, and P_{in} is the intensity of incident light (e.g., in W/m² or Mw/cm²). V_{oc} is the open-circuit voltage, J_{sc} is the short-circuit current density, and fill factor (FF) is calculated from the values of V_{oc} , J_{sc} , and the maximum power point, P_{max} . All fabrication steps and characterization measurements

were carried out in an ambient environment without a protective atmosphere. While measuring the current density-voltage (J-V) curves for DSSCs, a black mask was used and only the effective area of the cell was exposed to light irradiation. The data reported in this paper was confirmed by making each device more than 5 times.

3. Results and Discussion

Scheme 1 shows three different polymerization routes between the diazide- and diethynyl-based monomers. The molecular structures of the fluorene-based monomers with diazide and diethynyl units are published elsewhere.⁷⁻⁹ The desired 1,4-disubstituted 1,2,3-triazole ring units were introduced into the fluorene-based polymer backbone using 2,7-diazido-9,9-dioctylfluorene monomer by click coupling with 2,7-diethynyl-9,9-dioctylfluorene at 1:1 mol. equivalent ratio using three different methods such as catalysts, non-catalyst and catalyst with end-capping. Polymers P1, P2, and P3 were obtained from the above three different methods, respectively. In order to improve the purity of the polymers and photovoltaic performance, the precipitated polymers were further purified and highly purified polymers were obtained. The resulting polymers were completely soluble in various organic solvents. Table 1 summarizes the polymerization results, molecular

Table 1. Polymerization results and thermal properties of P1-P3.

Polymers	Yield (%)	M _w ^a (x10 ⁻³)	PDI ^a	DSC	TGA ^b
P1	92	16	1.9	115	339
P2	91	16	2.2	104	362
P3	94	33	2.4	97	346

^aMeasured by GPC using polystyrene standards.

^bMeasured at temperature of 5% weight loss for the polymers.

weights and thermal characteristics of the polymers. The weight average molecular weight (M_w) and polydispersity of the polymers ranged from (16-33) $\times 10^3$ and 1.9-2.4, respectively.

The GPC results revealed these polymers to have a relative narrow polydispersity index. These polymers had a better solubility in the reaction system due to the long alkyl side chain. Therefore, the reagents can react with each other in a manner to afford a narrow molecular weight distribution. The structure and thermal properties of the polymers were identified by $^1\text{H-NMR}$, infrared spectroscopy, elemental analysis, DSC, and TGA thermograms. The appearance of the characteristics of the 1,4-disubstituted 1,2,3-triazole peaks from the polymers at approximately 8.39-8.03 ppm in $^1\text{H-NMR}$ and the acetylenic proton peaks 2100 cm^{-1} in infrared spectroscopy, confirmed the polymerization reaction. The other peaks were consistent with the proposed chemical structure of the polymers. The thermal stability of the polymers was determined by TGA under a N_2 atmosphere. As shown in Table 1, isothermal pyrolysis showed that the 1,4-disubstituted 1,2,3-triazole units were lost at approximately $362\text{ }^\circ\text{C}$ followed by polymer decomposition at higher temperatures. The thermally induced phase transition properties of the polymers were also examined by DSC under a N_2 atmosphere. Most fluorene-based functional polymers do not show a distinct glass transition temperature (T_g). However, the T_g of the polymers ranged from $97\text{-}115\text{ }^\circ\text{C}$. These values are higher than those of poly(9,9-dioctylfluorene)¹⁷ and poly(9,9-dihexylfluorene).¹⁸ It is evident that the incorporation of 1,4-disubstituted 1,2,3-triazole ring units in the main chain can increase the T_g of the resulting fluorene-based polymers. This is very important if these polymers are to be used as active materials for electronic applications such as PLEDs, OPVs, and DSSCs. The absorption and PL data of

the polymers were measured in both solution and film states, and the optical properties are summarized in Table 2. The UV-visible absorption spectra of the polymers in chloroform and in thin films coated onto the quartz substrates were examined. In solution state, P1-P3 showed absorption maxima at 350, 337, and 351 nm, respectively, as shown in Figure 1(a). Among the polymers, P2 showed a significantly different peak in solution compared with the other polymers. Since, P2 was synthesized by non-catalyst click reaction methods. As shown in Figure 1(b), the UV-visible absorption spectra of film states were similar in solution with a similar maximum absorption wavelength. This indicates a similar conformation of the polymers in both states with tailing structures in the low energy regions in front of steep main absorption band edges.

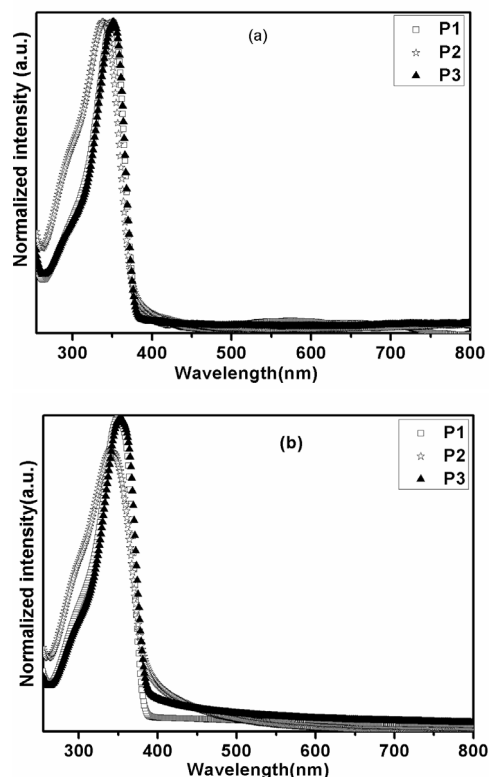


Figure 1. UV-visible absorption spectra in chloroform (a) and film (b) of P1-P3.

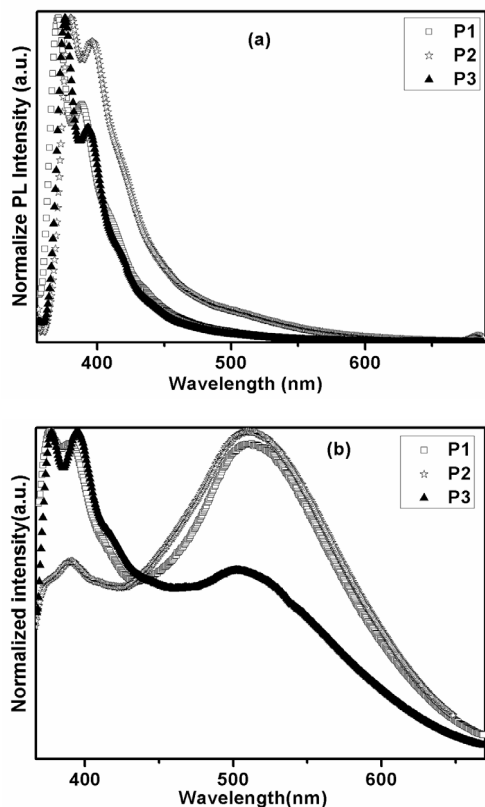


Figure 2. PL emission in solution (a) and film (b) of P1-P3.

Figure 2 shows the PL spectra of the polymers, in chloroform solution and in the thin film state. The PL spectra of the polymers in chloroform were similar and emitted a blue color between 370 and 395 nm as shown in Figure 2(a), which can be explained using fluorene moiety induced emission bands.

In addition to these blue bands, P1, P2 and P3 has pronounced energetically lower lying structureless bands centered at approximately 512 nm. This can be explained by the introduction of 1, 2, 3-triazole units with narrow polydispersity in the polymer chain. As shown in Figure 2(b), the PL spectra of the polymers in film states are quite different compared with the solution states. The emission spectra of P1-P3 in the solid films were slightly red-shifted by 15-40 nm, and had a significantly pronounced en-

ergetically lower lying band centered at approximately 535 nm. This red-shift can often be explained by the formation of an interchain excimer. The most dramatic change was observed in the film PL spectrum of P2. P2 had a maximum emission peak at 510 nm with a residual blue band at 390 nm, which were attributed to the non-catalyst click reaction condition (polar solvent DMF/toluene) and fluorene units, respectively. The PL spectrum of P1 and P3 were almost similar, but P1 had a strong emission peak at 512 nm whereas P3 had a shoulder peak at 503nm. This indicates that the copper catalyst dominates the luminescence properties of these polymers in its solid state through an energy transfer effect due to the perfectly overlapped blue emission band and absorption band.

Redox measurements were carried out using CV to determine the electrochemical properties of the polymers and to evaluate their HOMO and LUMO energy levels and results are summarized in Table 2. The HOMO binding energies of the polymers with respect to the ferrocene/ferrocenium (4.8 eV) standard were approximately 5.75 eV for P1, 5.67 eV for P2, and 5.62 eV for P3. From the onsets of the absorption spectra, the band gaps of P1-P3 were calculated to be 2.56, 2.39, and 2.32 eV, respectively. The LUMO energy levels were calculated from the band

Table 2. Electro-optical properties of P1-P3

Click Polymers	Abs (nm)	PL (nm)	Eg ^a (eV)	HOMO (eV)	LUMO (eV)
P1	348	375, 390, 511	2.56	5.75	3.19
P2	340	390, 510	2.39	5.67	3.28
P3	352	376, 394, 503	2.32	5.62	3.30

^aMeasured from UV-visible absorption film state.

gaps and HOMO energies. It was reported that the HOMO and LUMO energy levels of poly (9,9-dioctylfluorene) measured using an electrochemical method were 5.8 eV and 2.12 eV, respectively.¹⁹ There is a significant difference in electrochemical behaviour between the reported data and present polymers, which suggests that the electrochemical properties of the polymers had been altered through the introduction of a 1,4-disubstituted 1,2,3-triazole group between the fluorene units along with the polymer backbone via different click reactions.

The HOMO, LOMO energy level and band gap of these polymers were significant different due to synthetic method of the polymers.

Figure 3 shows the J-V curves of a SnO₂:F/TiO₂/N₇₁₉ Dye/solid-state electrolyte/Pt device using P1-P3 as the polymer matrix for the solid-state electrolyte under AM 1.5G illumination (100 mW/cm²). Table 3 are summarized the photovoltaic properties of the DSSCs. The solid-state DSSCs exhibited photovoltaic performances with power conversion efficiency (PCE) of 4.62 %, 4.41 %, and 4.02 % for P1, P2 and P3, respectively.

P3 shows the lower short-circuit current density and PCE than P1 and P2. It is due to higher molec-

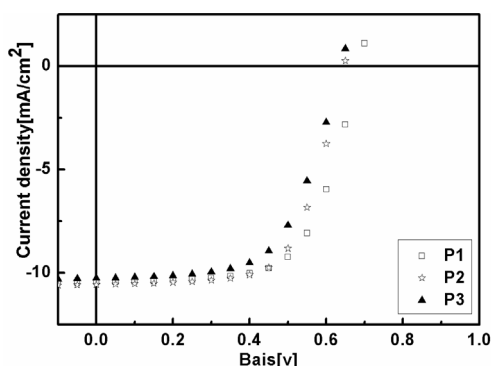


Figure 3. I-V curve of the DSSCs fabricated with P1-P3 as a polymer matrix of solid-state electrolyte under AM 1.5 sunlight illumination (100 mW/cm²).

Table 3. Photovoltaic properties of the DSSCs made with P1-P3

DSSCs with click polymers	J _{sc} (mW/cm ²)	V _{oc} (V)	FF (%)	PCE (%)
P1	10.46	0.65	68.0	4.62
P2	10.56	0.60	69.6	4.41
P3	10.25	0.60	65.4	4.02

ular weight of P3 and polymerization method. On the other hand, the decrease in the J_{sc} of DSSC with P3 electrolyte is mainly originates from the lowered I₃⁻ diffusion coefficients, which reduce the supply of I₃⁻ to the counter electrode, retard the regeneration of dye²⁰ and as a result lower the PCE. P1 shows the highest photovoltaic performance, which reached at 4.62 % under AM 1.5G illumination (100 mW/cm²) and slightly higher Voc than P2 and P3.

The higher photovoltaic performance of P1 was attributed to the low molecular weight, which allowed the solid-state electrolyte based on P1 to easily penetrate the dye adsorbed nanocrystalline porous TiO₂ electrode. The slight increase of Voc for the DSSC with P1 solid-state electrolyte may result from the polymerization method. Non-catalyzed click polymer P2 exhibited higher J_{sc} and FF than P1, but it performed lower PCE than P1. It's may be due to non-catalyzed click polymerization method and lower of Voc.

4. Conclusion

First time successfully employed the three different methods of click chemistry such as Cu^I-catalyzed, non-catalyzed and Cu^I-catalyzed with azide end-capping to synthesize fluorene-based functional polymers. The three different methods of 1,3-dipolar cycloaddition click reaction was employed between diazide- and diethynyl-fluorene to compare electro-optical as well as device performance and to find out the suitable reaction method for conjugated click

polymers. From the electro-optical properties and DSSCs device performance, it can conclude that the Cu^I-catalyzed 1,3-dipolar cycloaddition click reaction is an unique choice of click polymerization reaction.

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