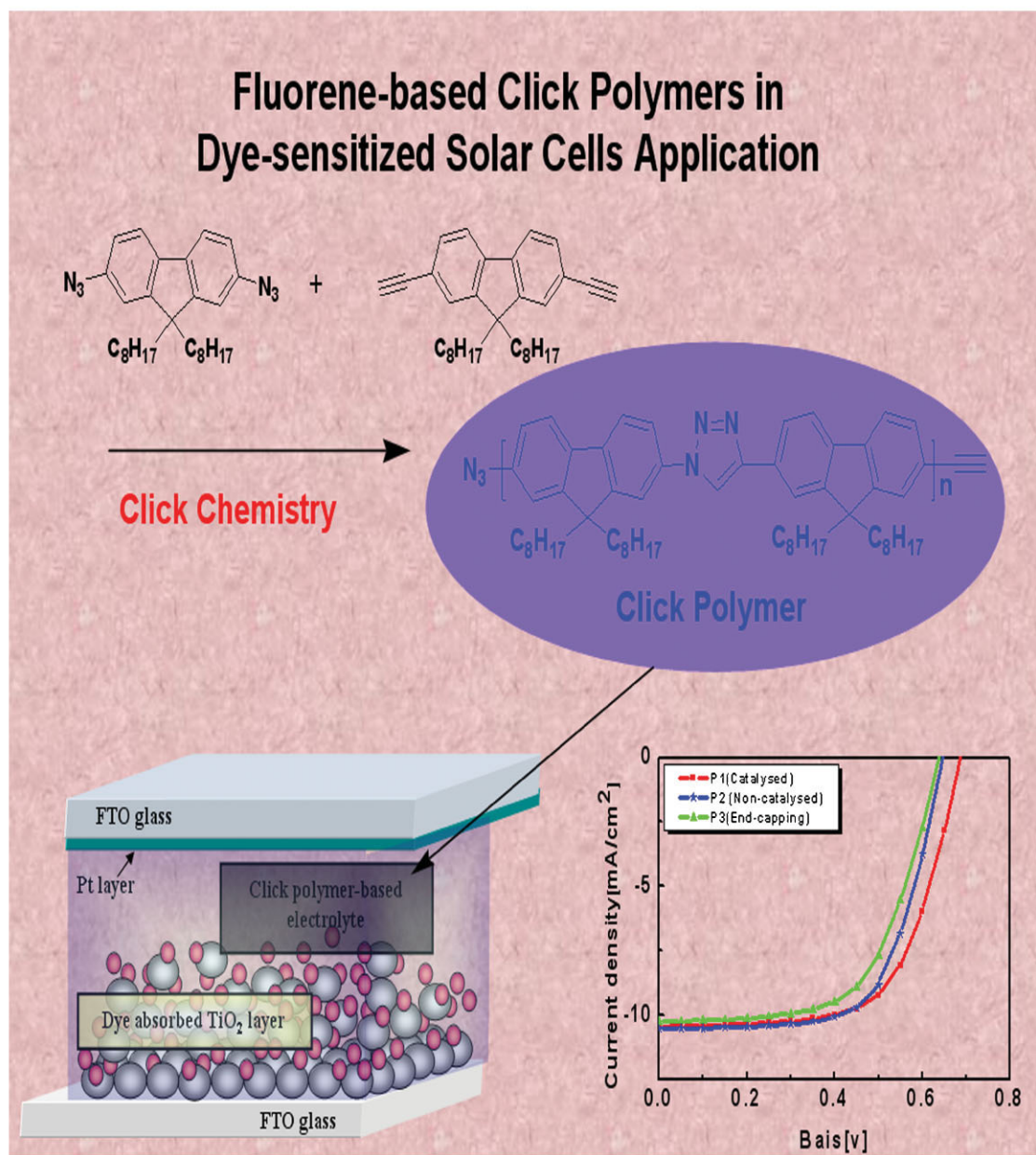


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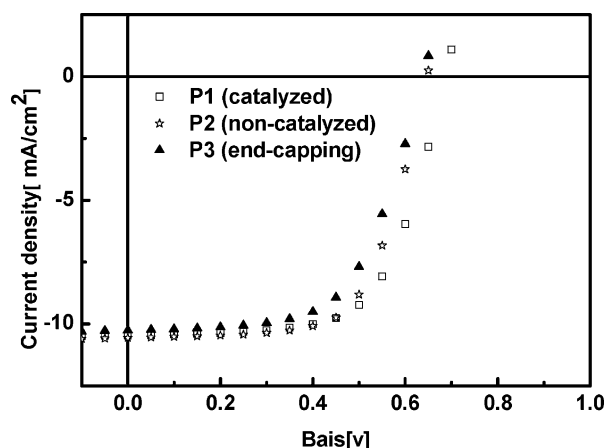
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Comparison of Three Different Click Reaction Methods for the Synthesis of Fluorene-Based Polymers and Performance in Quasi-Solid-State DSSCs

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The three different methods of click reaction has been used to synthesize fluorene-based click polymers and compared its effect on polymer electro-optical properties as well as photovoltaic performances in DSSCs. The DSSCs devices with configuration of $\text{SnO}_2\text{:F}/\text{TiO}_2/\text{N719 dye}/\text{quasi-solid-state electrolyte}/\text{Pt}$ devices were fabricated using these click polymers as a quasi-solid-state electrolyte components. Among the devices, the catalyzed click polymer composed DSSCs device exhibited high power conversion efficiency (PCE) of 4.62% under AM 1.5G illumination. These click polymers are promising materials for device application and the Cu^I -catalyst 1,3-dipolar cycloaddition click reaction is an efficient synthetic methodology.



Introduction

The 1,3-dipolar cycloaddition of an azide moiety and a triple bond has rapidly become the most popular click

reaction to date.^[1] The wide acceptance of this reaction can be attributed to 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 the presence of a large variety of functional groups. This methodology has been applied widely in organic chemistry,^[2] supramolecular chemistry,^[3] drug discovery,^[4] bioconjugation^[5] and materials science.^[6] Since the initial discovery of Cu^I catalyzed azide/alkyne coupling, numerous successful examples have been recorded, but as yet, no systematic study of optimal conditions has been reported for both catalyst^[7,8] and non-catalyst systems.^[9] To further understanding of the azide/alkyne click reaction, it is necessary to optimize the conditions under which the reaction is conducted to achieve high rates and yields with minimal synthetic manipulation.

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Polymer chemists have employed click chemistry to construct dendritic^[10] and linear macromolecules.^[11] The primary drawbacks of the polymers synthesized by click chemistry are long reaction times, poor product solubility^[7a,7b] and no optimized method. However, the synthesis of conjugated polymers by 1,3-dipolar cycloadditions has been conspicuously absent and only a few examples have been reported.^[7] There are many methods employed in 1,3-dipolar cycloaddition click reactions. The most popular methods are (1) copper catalyst with polytriazoles^[7a] or triethylamine (TEA)^[8,12] as Cu^I-stabilizing ligands, (2) copper catalyst without ligand,^[7b] and (3) non-catalyzed (using polar solvent with moderated temperature).^[9]

Among the reaction conditions of click chemistry, perhaps Cu^I-catalyzed 1,3-dipolar cycloaddition is the choice of reaction for chemists. However, it is very difficult to remove the metal completely from the resulting polymers. The catalyst residues can be detrimental to the electronic and optical properties of polymers, for example light emissions from conjugated polymers can be quenched by metallic traps.^[9] On the other hand, the 1,3-dipolar cycloaddition reaction involving azides and alkynes for the preparation of conjugated polymer shows the necessity of controlling the polymerization conditions because of the high reactivity of the azide and alkyne functionalities. One possible way to gain control and inhibit autopolymerization of the monomers is to put the functional groups in two separate monomers.^[13] To control autopolymerization, it may be necessary to end-cap in click polymerization.

In our previous work, we synthesized novel fluorene-based polymers using Cu^I-catalyzed azide/alkyne click coupling and the power conversion efficiency (PCE) was 2.80% in quasi-solid-state dye-sensitized solar cells (DSSC) with a configuration of SnO₂:F/TiO₂/N3 dye/quasi-solid-state electrolyte/Pt.^[8] From the above discussion of click polymerization methods and as an extension of our previous work, we have been interested in comparing the three methods in click polymerization such as (1) Cu^I-catalyzed 1,3-dipolar cycloaddition with alkylamine as ligand, (2) non-catalyzed (using polar solvent at moderate temperature), and (3) end-capping Cu^I-catalyzed 1,3-dipolar cycloaddition (azide end-capping). The current article focuses on the reaction method with the aim of improving the efficiency of the reaction conditions and its utility in future research. We have also compared the electro-optical properties and photovoltaic performance of these three click polymers, which were synthesized by the above mentioned methods. To date, since reported, we are the first to synthesize fluorene-based polymers using three different reaction methods in click chemistry.

Polymer gel electrolytes have some advantages, such as low vapor pressure, good long term stability, excellent contacting and filling properties between the nanostruc-

ture electrode and counter electrode, and higher ionic conductivity. Therefore, polymer gel electrolytes have been attracting intensive attention.^[14]

In this paper, our synthesized click polymers, P1–P3, are used as a polymer matrix to trap liquid electrolyte to form quasi-solid state electrolyte. The device was fabricated with the configuration SnO₂:F/TiO₂/N719 dye/quasi-solid-state electrolyte/Pt. The quasi-solid-state electrolyte was composed of I₂, tetrabutylammonium iodide (TBAI), 1-propyl-3-methylimidazolium iodide (PMII), ethylene carbonate (EC), propylene carbonate (PC), click polymers and acetonitrile. The effect of the click polymerization methods on the photovoltaic performance of the quasi-solid state DSSCs was studied.

Experimental Part

Materials and Characterization

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 of <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 columns 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⁻¹. Cyclic voltammetry (CV) was carried out using a Bioanalytical Systems CV-50W voltammetric analyzer at a potential scan rate of 50–100 mV · s⁻¹ 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⁻¹). A platinum wire and an Ag/AgNO₃ electrode were used as the counter and reference electrodes, respectively. All the electrochemical experiments were carried out in a glove box under an Ar atmosphere at room temperature.

Procedures for the Synthesis of Polymers

2,7-Diazido-9,9-dioctylfluorene^[15] and 2,7-diethynyl-9,9-dioctylfluorene^[16] were synthesized using a slight modification of the method reported in the literature.

Method (I) for the Synthesis of Polymer 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 triethylamine (TEA, 0.2–0.3 mL) added as a ligand to the mixture.^[8,12] 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 a 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 d 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 when 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.^[17] Polymer P1 was obtained as a yellow solid.

¹H NMR (CDCl₃): δ = 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).

(C₆₂H₈₂N₆)_n: Calcd. C 81.71, H 9.06, N 9.22; Found C 80.18, H 9.29, N 9.26.

Method (II) for the Synthesis of Polymer P2

In a flame dried Schlenk flask were placed diazide- and diethynyl-based monomers (1:1 equiv.) and an injected mixture of DMF/toluene (1:1 by volume). The reaction mixture was stirred under N₂ gas at 100 °C for 1 d. After this, the reaction mixture was diluted with chloroform and added dropwise to 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 a vacuum at room temperature.^[9] As no transition metal catalyst is used in the process, this polymerization enjoys such advantages as being less toxic, environmentally friendly and economically sounder. This helps simplify the reaction procedures and enhance the polymerization efficiency. Polymer P2 was obtained as a yellow solid.

¹H NMR (CDCl₃): δ = 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).

(C₆₂H₈₂N₆)_n: Calcd. C 81.71, H 9.06, N 9.22; Found C 80.18, H 9.29, N 9.26.

Method (III) for the Synthesis of Polymer P3

Diazide- and diethynyl-based monomers (1:1 equiv.) and sodium L-ascorbate (10 mol-%) were dissolved in THF (2–3 mL) under a flow of N₂ into a flame dried Schlenk flask and added to the mixture of triethylamine (2–3 mL) as a ligand.^[8,12] The flask was flushed with a flow of N₂ for 20–30 min and the mixture was frozen and evacuated three times. CuSO₄ · 5H₂O (5 mol-%) was then added

under a flow of N₂ gas. The mixture was allowed to stir at 30–35 °C for 48 h. A small amount of phenylacetylene was added as an azide end-capping material after checking the precipitation of the reaction mixture and stirring for a few more minutes. This study demonstrated the potential of the 1,3-dipolar cycloaddition reaction involving azides and alkynes for the preparation of conjugated polymer and also 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 autopolymerization of the monomers is to put the functional groups in two separate monomers.^[13] Therefore, to control the autopolymerization, the azide functional group of polymer end chain was end-capped by phenylacetylene. The THF was removed under a 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. Polymer P3 was obtained as a yellow solid.

¹H NMR (CDCl₃): δ = 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).

(C₆₂H₈₂N₆)_n: Calcd. C 82.96, H 8.75, N 8.29; Found C 81.41, H 8.97, N 8.33.

Fabrication and Measurement of DSSCs

The quasi-solid state electrolyte consisted of I₂ (1.15 M), TBAI (2.4 M) and PMII (3.95 M) in a co-solvent of EC and PC (0.4 mL, EC/PC = 3/1 w/w) 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 · cm⁻² of the transparent paste (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 to 60 °C at a controlled cooling rate (3 °C · min⁻¹) 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 DSSCs were measured using a calibrated AM 1.5G solar simulator (Orel 300 W simulator, models 81150) with a light intensity of 100 mW · cm⁻² adjusted using a standard PV reference cell (2 × 2 cm² 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 is given by:

$$\text{PCE} = P_{\text{out}}/P_{\text{in}} = (J_{\text{sc}} \times V_{\text{oc}}) \times \text{FF}/P_{\text{in}} \quad (1)$$

with

$$\text{FF} = P_{\text{max}}/(J_{\text{sc}} \times V_{\text{oc}}) = (J_{\text{max}} \times V_{\text{max}})/(J_{\text{sc}} \times V_{\text{oc}}) \quad (2)$$

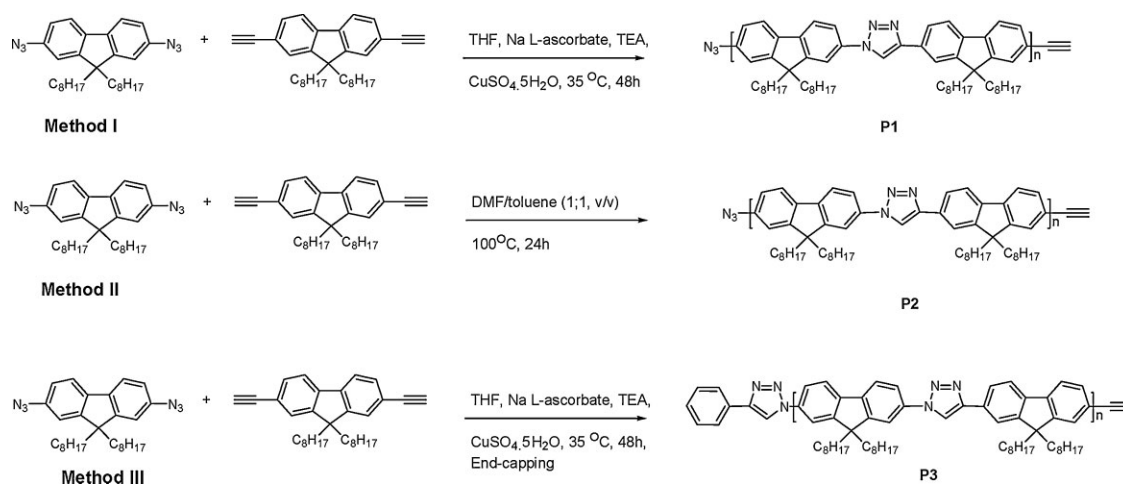
where P_{out} is the output electrical power of the device under illumination and P_{in} is the intensity of incident light (e.g., in $\text{W} \cdot \text{m}^{-2}$ or $\text{MW} \cdot \text{m}^{-2}$). V_{oc} is the open-circuit voltage, J_{sc} is the short-circuit current density, and the fill factor (FF) is calculated from the values of V_{oc} , J_{sc} , and the peak power, 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.

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.^[7,8] We first tried to synthesize these functional polymers using various methods of click chemistry and also measured electro-optical properties and compared photovoltaic performance in DSSCs. 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 a 1:1 mole 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 by multiple Soxhlet extraction with methanol, hexane and finally extracted with chloroform. From this process, a highly purified and narrow polydispersity of the polymers were obtained. The resulting polymers were completely soluble in various organic solvents such as chloroform, chlorobenzene, THF, toluene and xylene. Table 1 summarizes the polymerization results, molecular weights and thermal characteristics of the polymers. The weight-average molecular weight (\bar{M}_w) and polydispersity of the polymers ranged from $(16\text{--}33) \times 10^3$ and 1.9–2.4, respectively. The GPC results revealed these polymers to have a relatively 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 which affords a narrow molecular weight distribution.

The structure and thermal properties of the polymers were identified by ^1H 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 ^1H NMR and the acetylenic proton peaks at 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 Figure 1, isothermal pyrolysis showed that the 1,4-disubstituted 1,2,3-triazole units were lost at approximately 362°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



■ Scheme 1. Synthesis of polymers (P1–P3).

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

Polymers	Yield	\overline{M}_w ^{a)}	\overline{M}_n ^{a)}	M_p ^{a)}	PDI ^{a)}	T_g	TGA ^{b)}
	%					°C	°C
P1	92	16 118	8 386	12 090	1.92	115	339
P2	91	16 123	7 483	10 608	2.15	104	362
P3	94	33 360	13 817	20 543	2.41	97	346

^{a)}Measured by GPC using polystyrene standards, M_p = peak average molecular weight; ^{b)}Measured at temperature of 5% weight loss for the polymers.

fluorene-based polymers do not show a distinct glass transition temperature (T_g). However, the T_g of the polymers ranged from 97–115 °C. These values are higher than those of poly(9,9-dioctylfluorene)^[18] and poly(9,9-dihexylfluorene).^[19] It is evident that the incorporation of 1,4-disubstituted 1,2,3-triazole 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 polymer light-emitting diodes (PLEDs), organic photovoltaics (OPVs) and DSSCs. The higher thermal stability of the polymers prevents the deformation and degradation of the active layer from the heat induced during the operation of the devices.

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 the solution state, P1–P3 showed absorption maxima at 350, 337 and 351 nm, respectively, as shown in Figure 2(a). Among the polymers, P2 showed a significantly different peak in solution compared with the other

polymers, which was due to the synthesis of P2 by non-catalyst click reaction methods to form 1,2,3-triazole units in the polymer backbone. As shown in Figure 2(b), the UV-visible absorption spectra of the 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 3 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 3(a), which can be explained using fluorene moiety induced emission bands. These blue bands have well developed vibronic structures with approximately 130 meV vibronic band gaps, which are typical in such conjugated systems due to their carbon–carbon double bond stretching mode. These pronounced vibronic structures are common features of the film PL spectra. In addition to these blue bands, P1, P2 and P3 have 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 3(b), the PL spectra of the polymers in film states are quite different compared with those in 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 energetically lower lying band

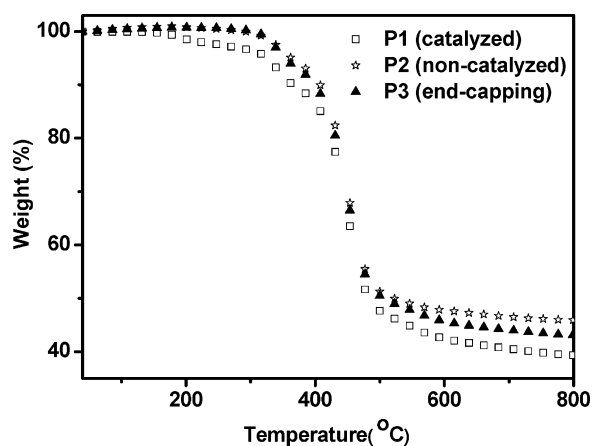


Figure 1. TGA thermograms of P1–P3 (at a heating rate of 10 °C · min⁻¹).

Table 2. Electro-optical properties of P1–P3.

Polymer	λ_{Abs}	λ_{PL}	E_g ^{a)}	E_{HOMO}	E_{LUMO}
	nm	nm	eV	eV	eV
P1	348	375, 390, 511	2.56	5.76	3.19
P2	340	390, 510	2.39	5.67	3.28
P3	352	376, 394, 503	2.32	5.62	3.30

^{a)}Measured from UV-visible absorption film state.

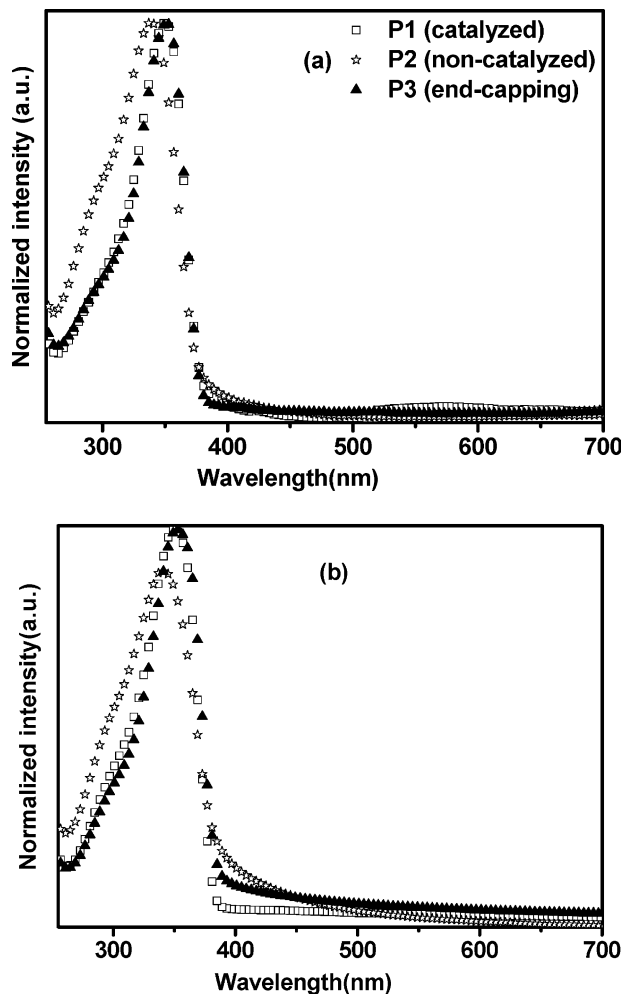


Figure 2. UV-vis absorption spectra (a) in chloroform (concentration 1.5×10^{-4} M) and (b) of films of P1–P3.

centered at approximately 535 nm. This red-shift can often be explained by the formation of an interchain excimer. Another possible explanation might be the strong reabsorption due to the relatively steep absorption edge where there is also an emission band for the $S_0 \leftarrow S_1$ 0–0 transition. 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 503 nm. 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 highest occupied molecular orbital

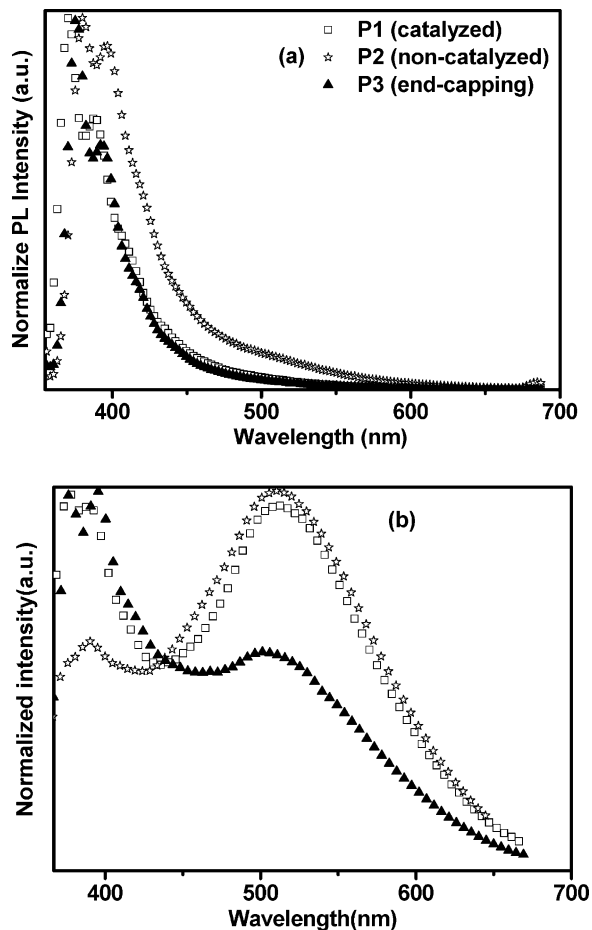


Figure 3. PL emission (a) in solution (concentration 1.5×10^{-4} M) and (b) of films of P1–P3.

(HOMO) and lowest unoccupied molecular orbital (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 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

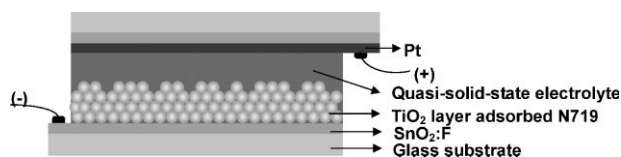


Figure 4. The cross-section structure of $\text{SnO}_2\text{:F}/\text{TiO}_2/\text{N719}$ dye/solid-state electrolyte/Pt devices.

and 2.12 eV, respectively.^[20] There is a significant difference in electrochemical behavior between the reported data and resulting 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 significantly different due to the synthetic methods of the polymers.

Figure 4 shows the device configuration of solid-state DSSCs using P1-P3 as the polymer matrix. Figure 5 shows the J/V curves of a SnO₂:F/TiO₂/N719 dye/quasi-solid-state electrolyte/Pt device using P1-P3 as the polymer matrix for the quasi-solid state electrolyte under AM1.5G illumination (100 mW·cm⁻²). Table 3 summarizes the photovoltaic properties of the DSSCs. The quasi-solid state DSSCs exhibited photovoltaic performances with PCE of 4.62, 4.41 and 4.02% for P1, P2 and P3, respectively. P3 shows the lower J_{sc} and PCE than P1 and P2. Due to the higher molecular weight of P3 compared to P1 and P2, the decrease in the J_{sc} of DSSC with P3 electrolyte mainly originates from the lowered I_3^- diffusion coefficients, which reduce the supply of I_3^- to the counter electrode, retard the regeneration of dye^[21] and, as a result, lower the PCE. P1 shows the highest photovoltaic performance, which reached 4.62% (V_{oc} : 0.65 V, J_{sc} : 10.46 mA·cm⁻², FF: 68.0) under AM1.5G illumination (100 mW·cm⁻²) and slightly higher V_{oc} than P2 and P3. The higher photovoltaic performance of P1 was attributed to the low molecular weight, which allowed the quasi-solid state electrolyte based on P1 to easily penetrate the dye adsorbed nanocrystalline porous TiO₂ electrode. Further developments of new electrolytes for better DSSC performance are currently underway.

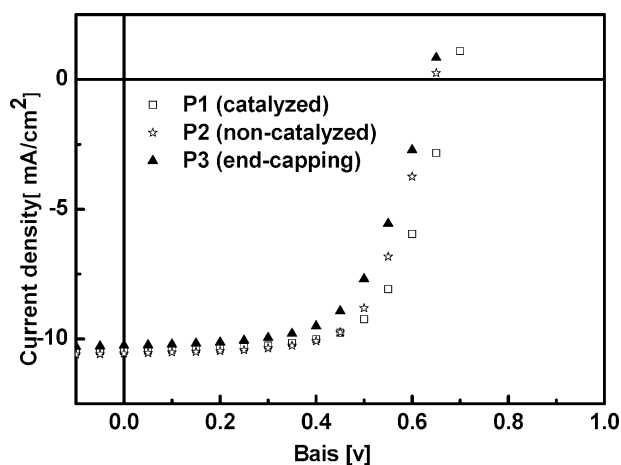


Figure 5. Photocurrent/voltage characteristics of the DSSCs fabricated with P1-P3 as a polymer matrix of solid-state electrolyte under AM1.5 sunlight illumination (100 mW·cm⁻²).

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

DSSC	J_{sc}	V_{oc}	FF	PCE	Area
	mA·cm ⁻²	V	%	%	mm ²
P1	10.46	0.65	68.0	4.62	21.003
P2	10.56	0.60	69.6	4.41	20.001
P3	10.25	0.60	65.4	4.02	22.161

Conclusion

For the first time, we have 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 polymers. The three different methods of 1,3-dipolar cycloaddition click reaction were employed between diazide- and diethynyl-based fluorene monomers to compare electro-optical as well as photovoltaic performance and to find a suitable reaction method for conjugated click polymers. From the absorption, emission, CV results and DSSC performance, we are able to conclude that the Cu^I-catalyzed 1,3-dipolar cycloaddition click polymer exhibited the highest PCE of 4.62% and better electro-optical properties than both the non-catalyzed and azide end-capping click polymers. Thus, we hope these results will help to extend the potential applications of the Cu^I-catalyzed click reaction and the click polymer as a new electronic materials for device in the future.

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