

Electronic Supplementary Information

Novel fluorene-based functional “click polymers” for quasi-solid-state dye-sensitized solar cells

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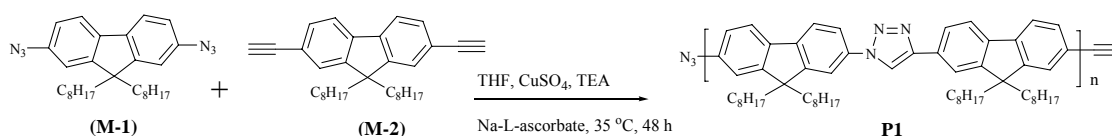
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Materials and Characterization

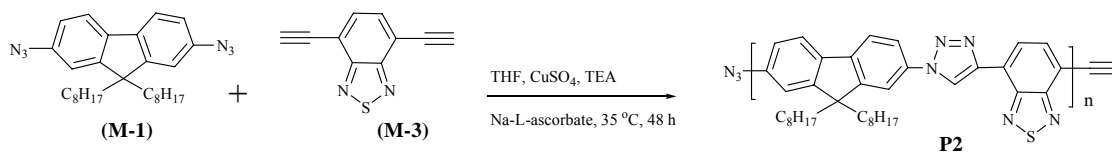
All used reagents were purchased from Sigma-Aldrich and used without further purification. Solvents were purified by normal procedures and handled under a moisture free atmosphere. Column chromatography was performed using silica gel (Merck, 250-430 mesh). Conventional Schlenk techniques were used and reactions were carried out under N₂ atmosphere unless otherwise noted. ¹H-NMR spectra were recorded on a Bruker AM-300 spectrometer and chemical shifts were recorded in ppm units with chloroform as an internal standard. UV-visible spectra were recorded with a Shimadzu UV-3100 spectrophotometer with a baseline correction and normalization carried out using Microsoft Excel software. The emission spectra for dilute solutions were determined using a Hitachi F-4500 fluorescence spectrophotometer. 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 less than 45°. Each polymer film was excited with several portions of visible light 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 with a Bioanalytical Systems CV-50W voltammetric analyzer at a potential scan rate of 50-100 mV/s in 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 the polymer solution (10 mg/mL). A platinum wire was used as the counter electrode, and an Ag/AgNO₃ electrode was used as the reference electrode. All of the electrochemical experiments were performed in a glove box under an Ar atmosphere at room temperature.

General procedure for the synthesis of polymers (P1-P4)

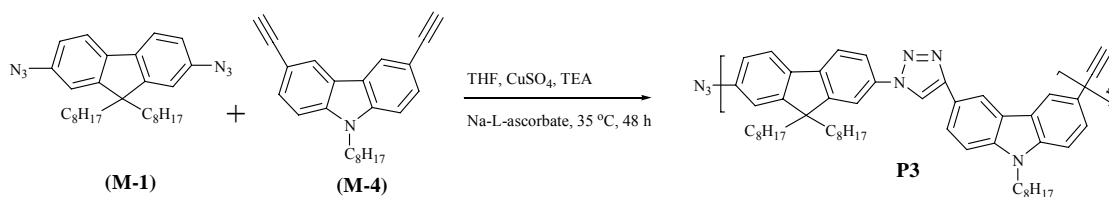
2,7-Diazido-9,9-dioctyl-fluorene (**M-1**),^{1,2} 2,7-diethynyl-9,9-dioctylfluorene (**M-2**),^{3,4} 4,7-diethynylbenzothiadiazole (**M-3**),⁵ N-octyl-3,6-diethynylcarbazole (**M-4**),⁶ 9,9-dipropargylfluorene (**M-5**),⁷ were synthesized using a slight modification of the method reported in the literature. 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 to a mixture of triethylamine (TEA) (0.2-0.3 mL) as a ligand.⁸ 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. 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. In order to improve the purity of the polymers and DSSC 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, xylene, and etc.



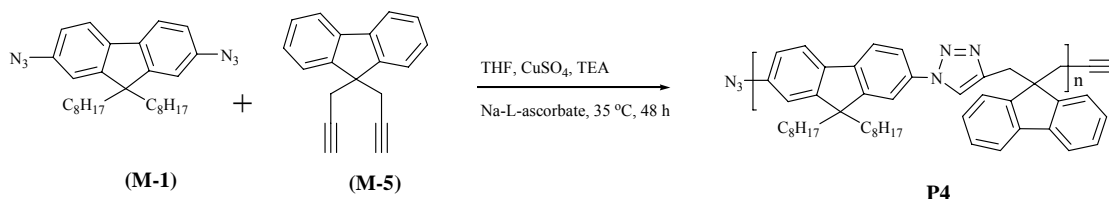
Polymer 1 (P1). [I+II], yellow solid. ¹H-NMR (CDCl₃, 500 MHz): δ (ppm) 8.39 (s), 8.35 (s), 8.03 (s), 7.95-7.91 (m), 7.86-7.79 (m), 7.78-7.73 (m), 7.09-7.07 (m), 7.03 (d), 2.19-2.10 (m), 2.05-1.99 (m), 1.27-1.10 (m), 0.95-0.78 (m), 0.72-0.66 (m). Anal Calcd for (C₆₂H₈₂N₆)_n: C, 81.71; H, 9.06, N, 9.22. Found: C, 80.18; H, 9.29; N, 9.26.



Polymer 2 (P2). [I+III], green-yellow solid. ¹H-NMR (CDCl₃, 300 MHz): δ (ppm) 8.87 (s), 7.91 (m), 7.83 (s), 7.75 (m), 7.03 (m), 2.11-2.04 (m), 1.26-1.11 (m), 0.85-0.66 (m). Anal Calcd for (C₃₉H₄₄N₈S)_n: C, 71.31; H, 6.75, N, 17.06, S, 4.88. Found: C, 69.97; H, 6.91; N, 17.13; S, 5.08.



Polymer 3 (P3). [I+IV], light yellow-brownish solid. $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ (ppm) 8.79 (s), 8.65 (s), 8.39 (s), 8.35 (d), 8.12 (d), 7.96-7.71 (m), 7.61-7.49 (m), 7.38 (s), 4.35 (d), 3.10 (s), 2.18-2.06 (m), 1.92 (d), 1.36-1.11 (m), 0.88-0.77 (m). Anal Calcd for $(\text{C}_{53}\text{H}_{65}\text{N}_7)_n$: C, 79.56.; H, 8.19, N, 12.25. Found: C, 78.07; H, 8.39; N, 12.30.



Polymer 4 (P4). [I+V], brown-yellow solid. $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ (ppm) 7.66 (s), 7.61 (s), 7.38 (s), 7.26-7.25 (m), 7.25-7.24 (m), 1.91 (s), 1.26-1.02 (m), 0.81-0.77 (m). Anal Calcd for $(\text{C}_{46}\text{H}_{50}\text{N}_6)_n$: C, 80.43; H, 7.34, N, 12.23. Found: C, 78.92; H, 7.52; N, 12.28.

The thermal stability of the **P1-P4** was determined by TGA under a N_2 atmosphere. As Fig. S1 shown that the 1,4-disubstituted 1,2,3-triazole units were lost at approximately 340 $^\circ\text{C}$ followed by polymer decomposition at higher temperatures.

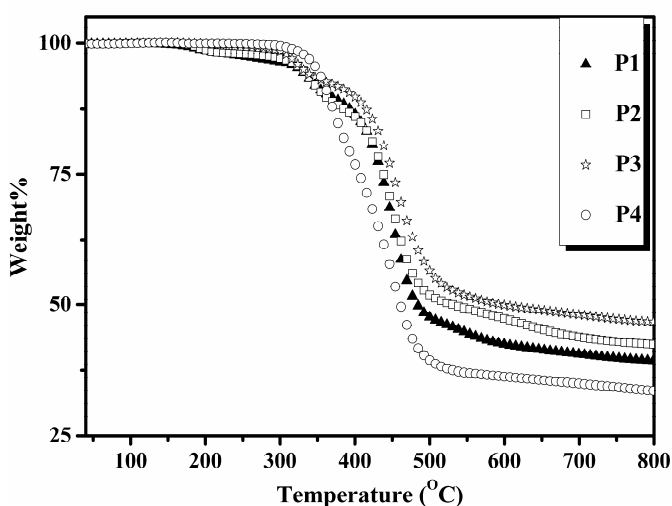


Fig. S1 TGA thermograms of **P1-P4** (at a heating rate of $10^0\text{C}/\text{min.}$)

Fabrication of DSSCs

The quasi-solid-state electrolyte consisted of I₂ (1.15 M), tetrabutylammonium iodide (TBAI) (0.23 M), and 1-ethyl-3-methylimidazolium iodide (0.39 M) in a cosolvent of ethylene carbonate (EC) and propylene carbonate (PC) (0.53 mL, EC/PC=4/1 as weight ratio) with **P1-P4** (50 mg) in an acetonitrile solution (0.4 mL). The gap between two electrodes was filled with the resulting hot solution using a vacuum pump. A uniform quasi-solid-state electrolyte layer was formed in the cells after cooling down to room temperature. The DSSCs were fabricated using N3 dye 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 N3 dye 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 quasi-solid-state electrolyte was cast onto the N3 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.

Notes and references

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