



Influence of different substituents linked on fluorene spacer in organic sensitizers on photovoltaic properties



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ABSTRACT

New metal-free organic sensitizers containing a fluorene unit as a π -conjugated system, a diphenylamine as an electron donor, and a cyanoacrylic acid moiety as an electron acceptor were synthesized and used for dye-sensitized solar cells. The photophysical and electrochemical properties of these dyes were investigated, and their performances as sensitizers in solar cells were measured. One solar cell containing the *n*-hexyl group in the fluorene unit produced an η of 5.15% ($J_{sc} = 9.69 \text{ mA cm}^{-2}$, $V_{oc} = 0.77 \text{ V}$, and $ff = 0.70$) under 100 mW cm^{-2} simulated AM 1.5 G solar irradiation (100 mW cm^{-2}).

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1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted significant attention in recent years because of their high efficiency, low cost, and facile fabrication [1–3]. DSSCs based on Ru(II)-polypyridyl complex photosensitizers, such as N3, N719, and the black dye, have achieved remarkable conversion efficiency of up to 11% under AM 1.5 irradiation conditions [4–6]. However, the main drawbacks of the Ru(II) complex sensitizers include the cost of ruthenium metal, the requirement for cautious synthesis, and the tedious purification process. Metal-free organic dyes have gained increasing attention because of their unique advantages, such as high molar absorption coefficient, ease of structure modification, and relatively low material cost [7–10].

A common organic dye for DSSCs contains a structure of electron donor/acceptor (D–A) that is linked through a π -conjugated bridge; this structure is called the D– π –A molecular structure [11]. In this structure, triphenylamine derivatives have been widely used as the electron donor (D), whereas a cyanoacrylic acid moiety acts as the electron acceptor (A). D– π –A dyes based on triphenylamine moieties with various π -conjugated bridges, such as benzene [12–18], thiophene [19–22], thienothiophene [23–27], dithienothio-

phene [28,29], benzo[*b*]thiophene [30,31], benzothiadiazole [32–35], or dibenzosilole [36] have been designed and synthesized as efficient sensitizers to achieve high conversion efficiency in DSSC devices. The π -conjugated bridge has a great influence on the photoelectronic properties of D– π –A dyes. Generally, some steric structures should be introduced to the π -conjugated bridge to inhibit unfavorable π – π aggregation [37]. However, the influence of different substituted groups on the π -conjugated bridge to avoid π – π aggregation has not been systematically studied.

This study presents three new organic dyes (**F1**, **F2**, and **F3**) with different group-substituted fluorene moieties as π -conjugated bridge, a diphenylamine moiety as electron donor, and a cyanoacetic acid as electron acceptor (Fig. 1). The study also investigates the photophysical, electrochemical, and photovoltaic properties.

2. Experimental section

2.1. General analytical measurements

All chemicals were used as received from commercial sources without purification. Solvents for chemical synthesis, such as dichloromethane, dimethylformamide, toluene, and tetrahydrofuran, were purified by distillation. 2,7-Dibromo-9,9-diphenyl-9H-fluorene [38] and 2,7-dibromo-9,9-dihexyl-9H-fluorene [39] were synthesized according to the reported literature. ^1H and ^{13}C NMR spectra were recorded on either Varian Inova-400 spectrometer

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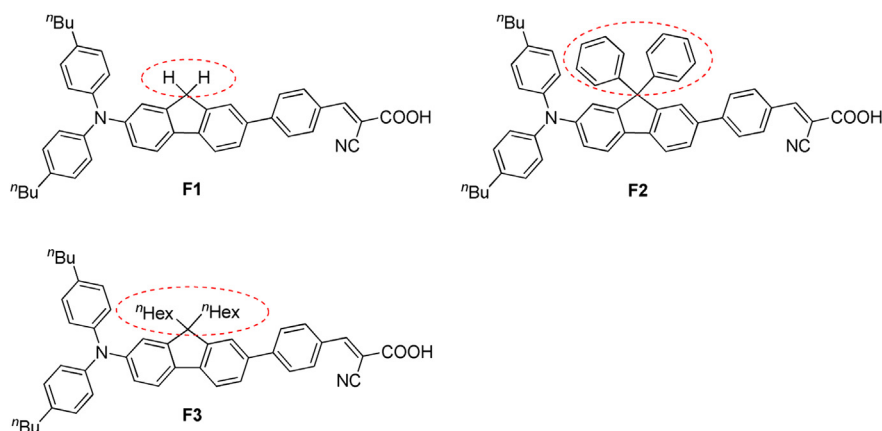


Fig. 1. Molecular structures of dyes **F1**, **F2**, and **F3**.

(400 MHz for ^1H ; 100 MHz for ^{13}C) or Bruker Avance II-400 spectrometer (400 MHz for ^1H ; 100 MHz for ^{13}C); CDCl_3 and TMS were used as solvent and internal standard, respectively. High-resolution mass spectra were recorded on either Q-TOF or GC-TOF mass spectrometer.

2.2. Theoretical calculations

Gaussian 03 package was used for density functional theory calculation [40]. The geometries and energies of **F1**, **F2**, and **F3** were determined using the B3LYP method with the 6-31G (d) basis set.

2.3. Synthesis

The synthetic routes to the **F1**, **F2**, and **F3** dyes are shown in Scheme 1.

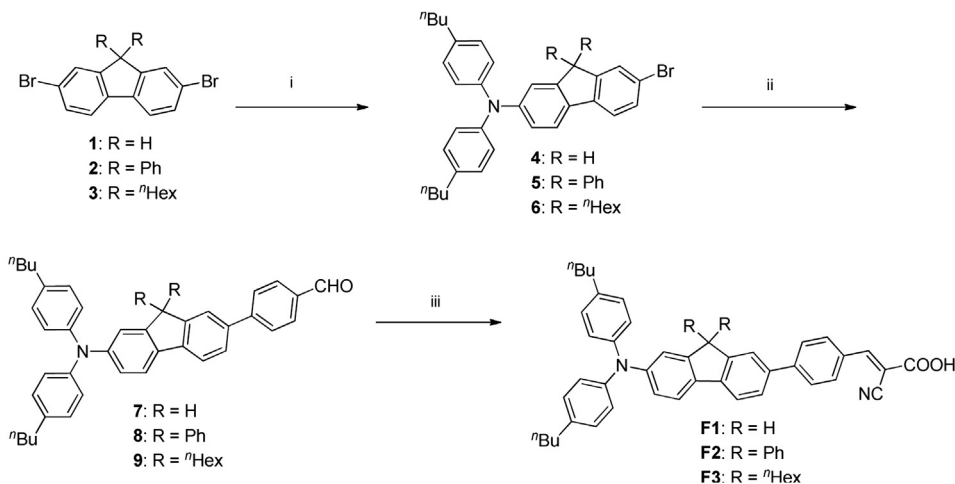
2.3.1. Synthesis of 7-bromo-*N,N*-bis(4-butylphenyl)-9*H*-fluoren-2-amine (**4**)

A mixture of bis(4-butylphenyl)amine (1.407 g, 5 mmol), 2,7-dibromo-9*H*-fluorene **1** (3.2401 g, 10 mmol), sodium *tert*-butoxide (0.961 g, 10 mmol), dppf (0.0641 g, 0.12 mmol), $\text{Pd}(\text{dba})_2$ (0.0575 g, 0.1 mmol), and toluene (80 ml) was refluxed under

nitrogen atmosphere for 24 h. After cooling to room temperature, water was added to quench the reaction. The product was extracted with dichloromethane (20 mL \times 3). The combined organic layers were dried over anhydrous MgSO_4 , and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica (petroleum ether/ethyl acetate = 100/1, v/v) to give a colorless oil **4** (1.2212 g, 2.33 mmol, 47%). ^1H NMR (400 MHz, CDCl_3) δ 7.58–7.53 (m, 2H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.43 (d, $J = 7.8$ Hz, 1H), 7.23 (s, 1H), 7.19 (s, 1H), 7.07–7.00 (m, 8H), 3.74 (s, 2H), 2.56 (t, $J = 7.6$ Hz, 4H), 1.61–1.56 (m, 4H), 1.40–1.34 (m, 4H), 0.94 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.9, 145.6, 145.0, 144.2, 140.7, 137.5, 134.7, 129.8, 129.2, 128.1, 124.4, 122.4, 120.4, 119.7, 119.3, 36.7, 35.1, 33.8, 22.5, 14.1. HRMS (EI): calcd. for $\text{C}_{33}\text{H}_{34}\text{NBr}$, 523.1875 $[\text{M}]^+$; found, 523.1870.

2.3.2. Synthesis of 7-bromo-*N,N*-bis(4-butylphenyl)-9,9-diphenyl-9*H*-fluoren-2-amine (**5**)

The synthetic route of **5** is similar with **4** to give a white solid in 63% yield. mp 168–169 $^\circ\text{C}$. ^1H NMR (400 MHz, d_6 -DMSO) δ 7.77 (dd, $J = 8.0$ Hz, 7.7 Hz, 2H), 7.55 (dd, $J = 8.1$ Hz, 3.4 Hz, 2H), 7.29–7.22 (m, 6H), 7.08 (d, $J = 8.4$ Hz, 4H), 7.02–6.84 (m, 10H), 2.56 (t, $J = 7.1$ Hz, 4H), 1.54–1.49 (m, 4H), 1.32–1.23 (m, 4H), 0.87 (t, $J = 7.3$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.7, 152.2, 148.4, 145.3, 145.2, 139.3,



Scheme 1. The synthetic routes for **F1**, **F2** and **F3** dyes: i) bis(4-butylphenyl)amine, $\text{Pd}(\text{dba})_2$, dppf, $t\text{BuONa}$, toluene, 110 $^\circ\text{C}$; ii) (4-formylphenyl)boronic acid, $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , THF, refluxed; iii) cyanoacetic acid, NH_4OAc , glacial CH_3COOH , refluxed.

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