

Synthesis and Characterization of Photoluminescent Copolymer Containing 1,1'-Binaphthyl and Fluorene Rings

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ABSTRACT: The luminescent polymer, F-DMBN, containing 2,2'-dimethacrylanido-1,1'-binaphthyl (DMBN) and 9,9-diphenylfluorene, is synthesized by the Heck reaction of halogenated and olefinic monomers. The structures are characterized by MS, ¹H-NMR, and IR, and the photoluminescent properties are investigated by UV/vis absorption and fluorescence spectra. The results show that the polymer emits blue and blue-violet light. The luminescence quantum yield is 0.424 in ethanol and the emission spectra exhibit obvious solvent effects. In addition, the light emitting can be

quenched by both electron donor (*N,N*-dimethylaniline) and electron acceptor (fullerene), where the processes follow the Stern–Volmer equation. Moreover, the interaction between F-DMBN and carbon nanotubes is also studied by fluorescent quenching. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 434–438, 2005

Key words: conjugated polymers; luminescence; monomers; fullerenes; Heck reaction

INTRODUCTION

Photoluminescent (PL) devices based on polymeric materials have received considerable attention in recent years since the discovery of photoluminescent conjugated polymer in 1990 by a Cambridge group.¹ Although a great deal of polymers have been synthesized and investigated, the search for new polymers with high performance remains a big challenge in this area.^{2–7} Ideally, these polymers should possess high PL efficiency, high stability, good processability, suitable conductivity, and low cost. To meet most of these requirements, copolymerization of two functional monomers may be a useful approach.

Fluorene derivatives show unique chemical and physical properties because they contain a rigid planar biphenyl unit, and the facile substitution at the C₉ position of fluorene can improve the solubility and processability of polymers containing fluorene without significantly increasing steric interactions in the polymer backbone.⁸ As a result, homopolymers and copolymers of fluorene have emerged as the most attractive blue-emitting materials due to their high efficiency and good thermal stability.^{9–11} 1,1'-Binaphthyl species have a twisted molecular structure, which could have a potential application in wavelength-sta-

ble light-emitting material.¹² Therefore, the synthesis of light-emitting polymers containing fluorene units and 1,1'-binaphthyl units is necessary for fabricating highly efficient and stable polymer light-emitting diodes (LEDs).

In this paper, we report the synthesis and characterization of a novel copolymer consisting of 9,9-diphenylfluorene moieties, which have high luminescent efficiency and good thermal stability, and 2,2'-dimethacrylanido-1,1'-binaphthyl (DMBN) moieties, which emit blue fluorescence with high quantum yield. The PL of the copolymer is examined in different solvents. Moreover, the molecular interactions of copolymer with *N,N*-dimethylaniline (DMA), fullerene (C₆₀), and carbon nanotubes (CNTs) are investigated.

EXPERIMENTAL

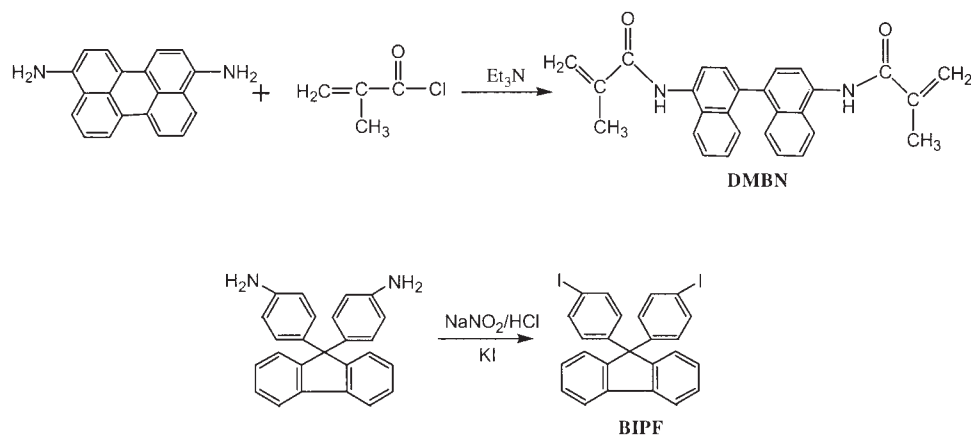
Materials and instruments

The reagents and chemicals for preparation of monomer and polymer are used as received unless noted otherwise. Ethanol, acetonitrile, acetone, THF, toluene, and benzene were purchased from Beijing Chemical Plant and treated according to standard methods used before, which are all applied to measurement of the light-emitting properties. The synthetic routes used are shown in Schemes 1 and 2.

Melting points were determined on a Sanyo Gallenkamp MPD350 melting point apparatus and were uncorrected. The IR spectra were determined on a PE-1700 IR spectrophotometer by dispersing samples in KBr disks. ¹H-NMR spectra were measured on a Bruker ARX300 spectrometer with DMSO as solvent.

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Scheme 1 The synthesis of monomers (DMBN, BIPF).

Mass spectrum dates were obtained on a JEOL GC-MS D300. UV-visible and fluorescence spectra were obtained on a Shimadzu UV-265 spectrophotometer and Shimadzu RF-540 spectrofluorotometer, respectively. The luminescence spectrometer has a xenon lamp as the light source. Both excitation and emission bands were set at 5 nm. All experiments were carried out at $20 \pm 1^\circ\text{C}$.

Synthesis of monomers (Scheme 1)

DMBN monomer¹³

DMBN was synthesized by amidation reaction between 1,1'-binaphthyl-2,2'-diamine and methacryloyl chloride in the presence of triethylamine.

9,9-bis(4'-iodophenyl)fluorene (BIPF) monomer¹⁴

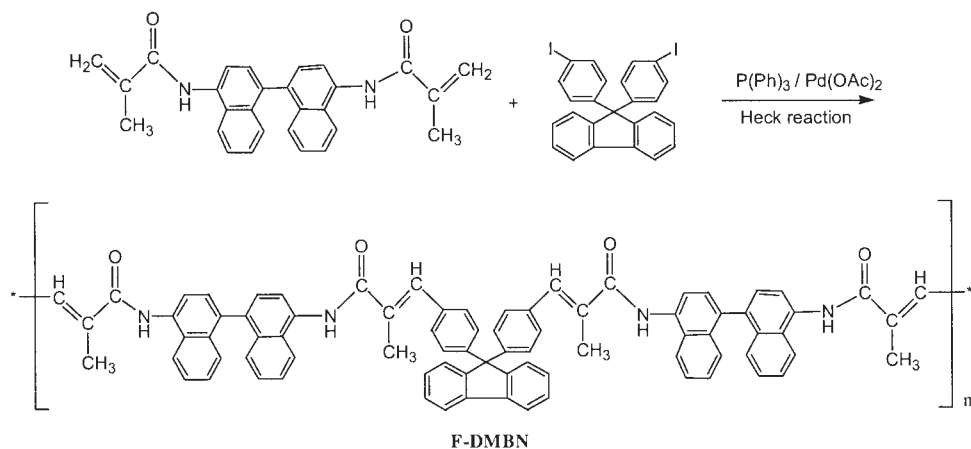
9,9-Bis(4'-aminophenyl)fluorene (0.7 g, 2.0 mmol) and concentrated hydrochloric acid (5 mL) were refluxed for 2 h and then cool to room temperature. The mixture with phosphoric acid (7 mL), sodium nitrite (0.274

g, 4.0 mol), and concentrated sulfuric acid (3 mL) was stirred at -5°C for 0.5 h. A solution of urea (0.3 g) and potassium iodide (0.664 g, 4.0 mmol) in water (50 mL) was poured into the reaction mixtures and the reaction system was heated with stirring until bubbles were no longer generated. The precipitate was obtained by adding 40 mL water; it was then dissolved by ethanol. After the insolubles were filtered off, the remaining liquid was poured into water, giving a white solid. The pure product, BIPF, was given in 81.5% yield by recrystallization from anhydrous ethanol: m.p., $183\text{--}184^\circ\text{C}$; MS (EI, m/z), 570(M^+); $^1\text{H-NMR}$ (DMSO, ppm): δ , 7.72–7.35 (16H, aromatic); IR (KBr, cm^{-1}): 1601, 1575, 1483, 1446 (\odot), 802 (\ominus), 484 (C-I).

Synthesis of polymer (Scheme 2)

Polymer (F-DMBN)¹⁵

Anhydrous palladium acetate (0.0112 g, 0.05 mmol), 9,9-bis(4'-iodophenyl)fluorene (1.45 g, 2.5 mmol), sodium acetate (0.4 g, 5 mmol), and 2,2'-dimethacrylamido-1,1'-binaphthyl (1.05 g, 2.5 mmol) were dis-



Scheme 2 The synthesis of polymer (F-DMBN).

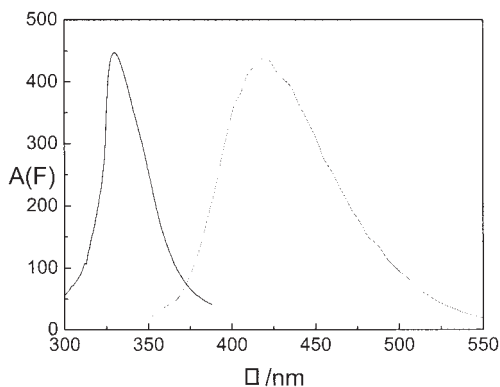


Figure 1 Absorption and emission spectra of F-DMBN in acetone. Concentration of F-DMBN, 2.98×10^{-2} mg/mL.

solved in 300 mL dry DMF and stirred at 140°C under a nitrogen atmosphere for 48 h. The water (200 mL) was added into the reaction mixture and the precipitate was collected by filtration. The brown solid was dissolved by ethanol and poured into 300 mL distilled water. The solid product was collected by filtration and purified by column chromatography on silica gel with ethyl acetate:petroleum ether (1 : 3) as the eluant to give in 25.4% yield slightly brown-red crystals. $^1\text{H-NMR}$ (DMSO, ppm) δ : 7.92–7.27 (30H, aromatic), 2.89 (2H, 2-NH-), 1.62 (6H, 2-CH₃); IR (KBr, cm^{-1}): 3415 (-NH-), 1654 (C = O), 1602 (C = C), 1595, 1525, 1498, 1436 ($\text{C}=\text{C}$), 1388 (-CH₃).

RESULTS AND DISCUSSION

The details of synthesis

BIPF could be obtained via the diazotization reaction by employing $\text{NaNO}_3/\text{H}_2\text{SO}_4/\text{KI}$. The DMBN is synthesized by amidations between 1,1'-binaphthyl-2,2'-diamine and methacryloylchloride in the presence of triethylamine. The polymer (F-DMBN) is prepared by the Heck reaction of 9,9-bis(4'-iodophenyl)fluorene and 2,2'-dimethacrylanido-1,1'-bi-naphthyl. Although this is a well-established method for C-C bond formation, the contents of catalyst and reaction temperature have a significant influence on the Heck reaction. It has been found by experiment that the appropriate ratio of $\text{Pd}(\text{OAc})_2$ to $\text{P}(\text{Ph})_3$ is 1 : 4 (mol), which can successfully form the reactive catalyst. The suitable reaction temperature is 140°C .

Comparing the IR spectrum of F-DMBN with that of BIPF evidences the formation of the designed polymer. The most obvious change of the IR after the Heck reaction is the appearance of a new peak at ca. 1654 cm^{-1} , which indicates that the C = O structure is introduced into the copolymer, F-DMBN. In addition, the disappearance of 484 cm^{-1} ($\text{C}=\text{C}$) and the appear-

ance of 1602 cm^{-1} ($\text{C}=\text{C}$) indicate that the F-DMBN is successfully synthesized by the Heck reaction.

Absorption and fluorescence emission spectrum

The UV/vis absorption and fluorescence emission spectra of F-DMBN in acetone are shown in Figure 1. It can be seen from Figure 1 that the maximum absorption and emission peaks of F-DMBN are at 333 and 420 nm, respectively. This shows that the polymer emits blue and blue-violet light and is a desirable blue-emitting photoluminescence material.

Quantum yield of photoluminescence

The fluorescence quantum yield is measured by the relative method using quinine sulfate as standard (0.546 in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$).¹⁶ The quantum yield is calculated from the equation

$$\Phi_s = \Phi_r \frac{F_s A_r}{F_r A_s} \left[\frac{n_r}{n_s} \right]^2$$

In the above expression, ϕ_s is the fluorescent quantum yield, F is the integration of the emission intensities, n is the index of refraction of the solution, and A is the absorbance of the solution at the exciting wavelength. The subscripts r and s denote the reference and unknown samples, respectively. The values of quantum yield of F-DMBN in different solvents are listed in Table I.

Solvent effect of photoluminescence

The fluorescence emission spectra of dilute solutions of F-DMBN are investigated in different solvents and all results are listed in Table I. It is noted that the fluorescent wavelength has a slight change in different solvents. This can be explained as follows: the molecular structure of F-DMBN has rigid aromatic ring structure units; the interaction between the solvents and the F-DMBN molecules is not great enough to influence the effective conjugation segment in the polymer chain of F-DMBN. Therefore, the wavelength

TABLE I
The Maximum Emission Peaks and Quantum Yields of F-DMBN in Different Solvents

Solvent	$E_r(30)$	ε/n_D^{20}	$\lambda_{\text{max}}^{\text{em}}/\text{nm}$	Φ_s
Ethanol	51.9	18.03	416	0.424
Acetonitrile	46.0	27.89	419	—
Acetone	42.2	15.23	420	—
THF	37.4	5.39	421	0.305
Benzene	34.5	1.52	419	—
Toluene	33.9	1.59	417	0.219

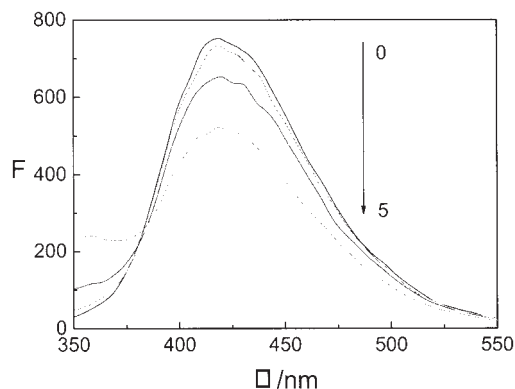


Figure 2 Fluorescence spectra of F-DMBN at different concentrations of DMA. Concentration of F-DMBN, 2.32×10^{-2} mg/mL; concentration of DMA (mol/L, M), 0, 0.00; 1, 1.07×10^{-3} ; 2, 2.42×10^{-3} ; 3, 5.11×10^{-3} ; 4, 9.81×10^{-3} ; 5, 1.65×10^{-2} .

of the fluorescence peaks is few of solvent-dependent. However, the emission intensities and the quantum yield in fluorescence spectra change with the polarity of solvents (Table I). It is suggested that there is one main nonradiation pathway for energy relaxation in the F-DMBN. That is the rotation of two naphthalene rings of 1,1'-binaphthyl around the C_1-C_1' bond. The change of quantum yield with various solvents used can be ascribed to the solvent molecule clathrating or intercalating into the screw-sense structure of the F-DMBN. Since the screw-sense structure could get inclusion with some solvent molecules, the solvents used have a great influence on the rotation of the 1,1'-binaphthyl, which is directly related to fluorescent intensity and quantum yield. Different solvent molecules have different abilities to enter into the screw-sense structure of the F-DMBN molecule, leading to the appearance of solvent-dependence of the fluorescent intensity and the quantum yield.

The quenching process of fluorescence of F-DMBN with DMA

DMA is a typical electron donor. Hence, the studies of interactions between F-DMBN and DMA are helpful in understanding the optical electronic properties of F-DMBN. Figure 2 shows the emission spectra of F-DMBN in THF with different concentrations of DMA. From Figure 2, we can see that the fluorescence of F-DMBN is efficiently quenched and the quenching process follows the Stern-Volmer equation $F_M^0/F_M = 1 + K_{sv}[Q]$. The quenching coefficient, K_{sv} , is $2.77 \times 10^2 \text{ M}^{-1}$.

Interaction between F-DMBN and fullerene (C_{60})

Many investigations show that C_{60} is a good electron acceptor. It possesses a wide range of physical and

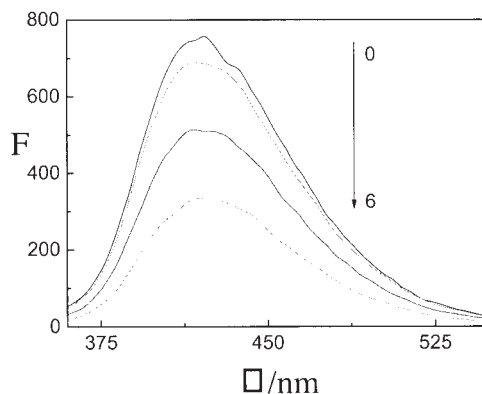


Figure 3 Fluorescence spectra of F-DMBN at different concentrations of C_{60} . Concentration of F-DMBN, 2.61×10^{-2} mg/mL; concentration of C_{60} (mol/L, M), 0, 0.00; 1, 2.38×10^{-7} ; 2, 6.35×10^{-7} ; 3, 1.43×10^{-6} ; 4, 2.22×10^{-6} ; 5, 3.42×10^{-6} ; 6, 5.01×10^{-6} .

chemical properties. One of the most remarkable properties of C_{60} is its ability to induce efficiently a rapid charge separation and a further slow charge recombination.¹⁷ In the experiment, the interactions of F-DMBN with C_{60} are examined. The results are shown in Figure 3. As we have seen in Figure 3, 0 is F-DMBN in concentration (2.61×10^{-2} mg/mL) without C_{60} , and 1–6 are F-DMBN in the presence of different concentration of C_{60} . With the gradual increasing of concentration of C_{60} , the fluorescence of F-DMBN is quenched efficiently and the process is also following the Stern-Volmer equation (Fig. 4). The apparent quenching constant is $3.65 \times 10^4 \text{ M}^{-1}$, which suggests that the strong interactions between F-DMBN and C_{60} happen in the excited state. This can be explained by the following reasons: both F-DMBN and C_{60} have a large π conjugated system in which π - π interactions may change the configuration of F-DMBN.¹⁸ Moreover, the photo-induced charge transfer from excited F-DMBN to C_{60} is rapid. Upon this charge transfer, the copolymer may be dramatically modified because of the strong electron-lattice inter-

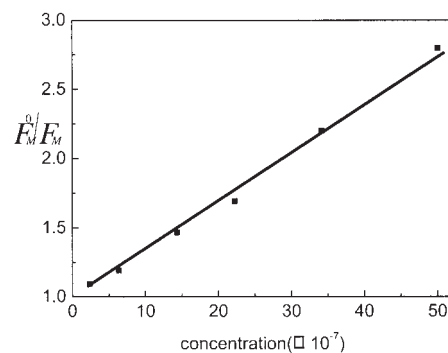


Figure 4 Dependence of F_M^0/F_M on the concentration of C_{60} . Concentration of F-DMBN, 2.61×10^{-2} mg/mL.

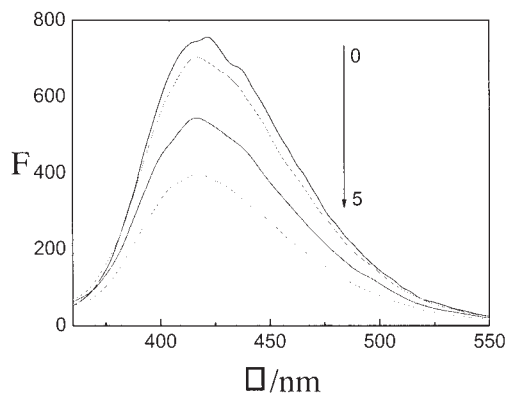


Figure 5 Fluorescence spectra of F-DMBN at different concentrations of CNTs. Concentration of F-DMBN, 2.75×10^{-2} mg/mL; concentration of CNTs (mg/mL), 0, 0.00; 1, 4.29×10^{-7} ; 2, 1.29×10^{-6} ; 3, 2.14×10^{-6} ; 4, 3.43×10^{-6} ; 5, 4.71×10^{-6} .

action in a one-dimensional system. In the system, the process of charge transfer from the π^* band of the photo-excited F-DMBN to C_{60} competes with the radiative emission of F-DMBN.

Interaction between F-DMBN and CNTs

The CNTs, just like the fullerenes, belong to an intriguing class of carbon materials. Due to the unique structures and cavity dimension scale of CNTs, it is meaningful to study their structural and charge transfer.¹⁹ In this paper, the interactions between F-DMBN and CNTs are investigated, which is helpful in understanding the optical property of F-DMBN and applying it to LEDs. The experiments show that the fluorescence of F-DMBN can be quenched by CNTs. The quenching process of F-DMBN with CNTs is shown in Figure 5. The interactions between F-DMBN and CNTs happen in the excited state, which may be caused by the photo-induced charge transfer and interactions of conjugating a π - π system. Further research toward a better understanding of this action is currently in progress.

CONCLUSIONS

In summary, the polymer F-DMBN, which has 1,1'-binaphthyl units and 9,9'-diphenylfluorene units, was synthesized by the Heck reaction. The structure is characterized and the photoluminescent properties were studied. The results show that the maximum absorption and emission peaks of F-DMBN are at 333 and 420 nm, respectively. The value of luminescent quantum yield is 0.424 in ethanol. Furthermore, the interactions between F-DMBN and fullerene or carbon nanotubes were investigated. The result indicates that the strong interactions are to appear between F-DMBN and C_{60} or CNTs at the excited states.

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