# Synthesis, Characterization, and Photophysics of a Novel Conjugated Polymer with 1,3,4-Oxadiazole, Carbazole, and Naphthalene Units

**Liheng Feng,[1] Xiaoju Wang,[2] Zhaobin Chen[1]**

[1]School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan, People's Republic of China 030006
[2]Key Laboratory of Chemical Biology and Molecular Engineering of the Ministry of Education, Institute of Molecular Science, Shanxi University, Taiyuan, 030006 People's Republic of China

**ABSTRACT:** A polymer containing 1,3,4-oxadiazole and carbazole units in the main chain and naphthalene moieties as side groups (P-OCN) was synthesized by the Wittig reaction of [2,5-bis(3-tolylene)1′,3′,4′-oxadiazole]-9-(α-naphthyl)-carbazole polymer (P-OCN). The optical properties were investigated with ultraviolet–visible absorption and fluorescence emission spectra. The results showed that the luminescence quantum yield of P-OCN was 0.673 in chloroform, and it emitted blue and blue-green light with a band gap of 3.49 eV estimated from the onset absorption. Thermogravimetric analysis and differential scanning calorimetry showed that the polymer exhibited good thermal stability up to 354°C with a glass-transition temperature higher than 110°C. To investigate the donating and accepting capacities of P-OCN, the fluorescent quenching technique was used to determinate the interactions between the polymer and the electron donor and electron acceptor. The results showed that the light emission could be quenched by both the electron donor (N,N-dimethylaniline) and electron acceptor (dimethylterephthalate). Furthermore, the interaction between P-OCN and fullerene was also studied with fluorescent quenching, and the processes followed the Stern–Volmer equation. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1995–2000, 2008

**Key words:** conjugated polymers; luminescence; monomers; photophysics; synthesis

## INTRODUCTION

Since the discovery of polymer light-emitting diodes based on poly(p-phenylenevinylene) by the Cambridge group, π-conjugated polymers have attracted much attention because of their good ability to form thin films, good mechanical properties, and excellent luminescence.[1,2] Many research efforts have been made to synthesize, characterize, and fabricate new π-conjugation polymers. Currently, one of the main research objectives in this field is to develop light-emitting polymers that exhibit both high light-emitting efficiency and high stability because these properties are directly related to the performance and reliability of light-emitting diodes. Additionally, the balance of the rates of electron injection and hole transport from apposite contracts into the device is crucial in achieving high photoluminescence (PL) efficiency.[3,4] 1,3,4-Oxadiazole-based compounds such as

2-(4′-biphenylyl)-5-(4′-*tert*-butylphenyl)-1,3,4-oxadiazole have been actually used as electron-injection materials to improve the balance of charge carriers and increase the photon/electron quantum efficiency.[5–12] Carbazole and its derivatives are prototypical hole-transporting molecules with strong absorption in the ultraviolet (UV) spectral region and blue-light emission.[13–18] In this study, we designed and synthesized a new conjugated polymer containing 1,3,4-oxadiazole and carbazole units in the main chain and naphthalene side groups (P-OCN). The photophysical processes of P-OCN were investigated carefully. The fluorescence quenching technique for studying the mechanism of the interaction between P-OCN and its quencher was applied to understand the optical property of P-OCN. The quenching processes of polymer P-OCN with an electron donor, N,N-dimethylaniline (DMA), or an electron acceptor, dimethylterephthalate (DMTP), were studied. Moreover, the molecular interaction of polymer P-OCN with fullerene (C$_{60}$) was also investigated.
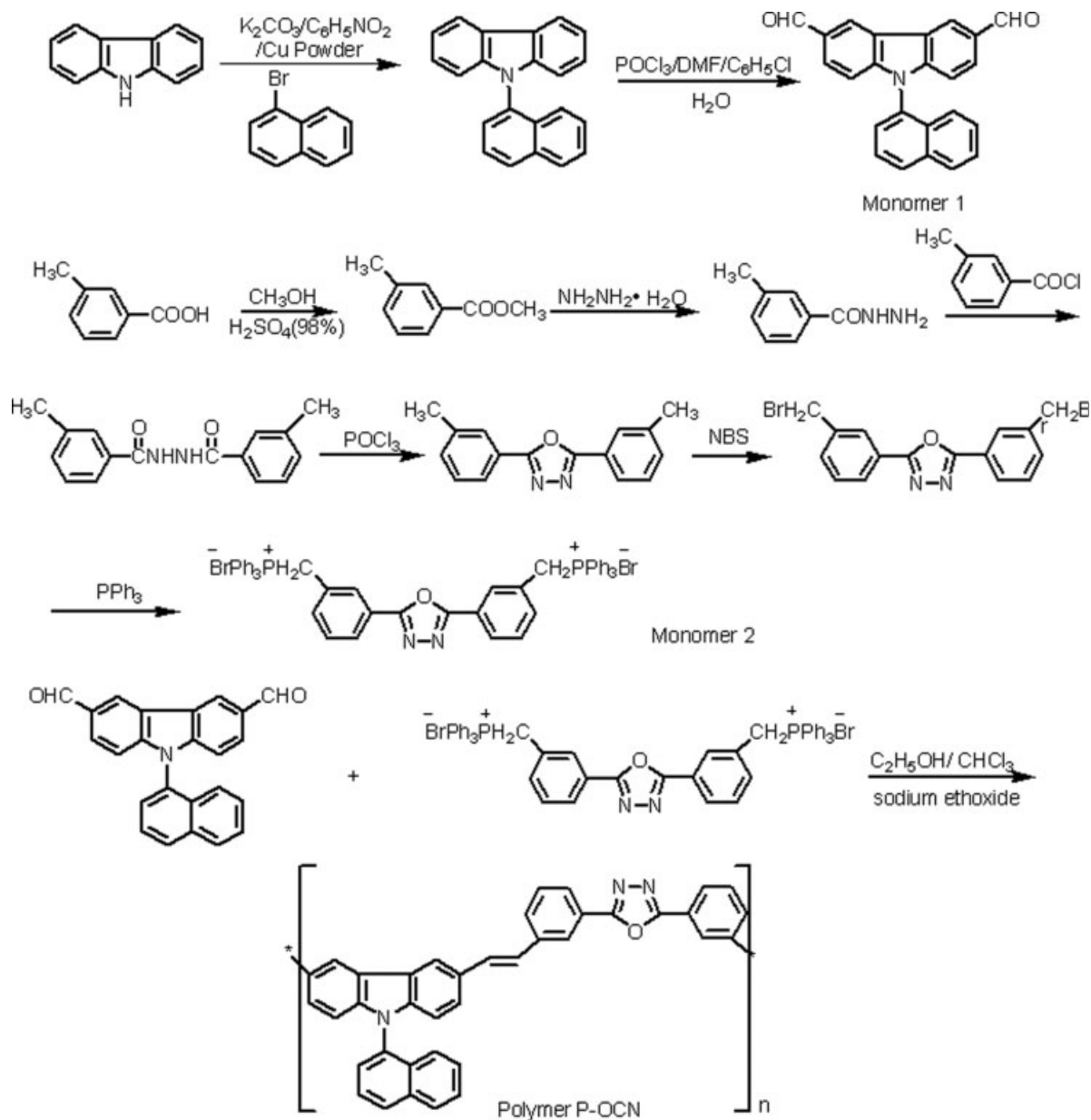
## EXPERIMENTAL

### Materials and instruments

The reagents and chemicals for the preparation of the monomers and polymer were used as received unless noted otherwise. Ethanol, dichloromethane,

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**Scheme 1** Synthesis routes of the monomers and polymer.

toluene, chloroform, ethyl acetate, petroleum ether, and so forth were purchased from Beijing Chemical Plant (Beijing, China) and treated according to standard methods used before, which were all applied to the measurement of the light-emitting properties. The synthesis route used is shown in Scheme 1.

Melting points were determined on a Sanyo Gallenkamp MPD350 melting-point apparatus (Leicestershire, UK) and were uncorrected. The IR spectra were determined on a PE-1700 IR spectrophotometer by the dispersion of samples in KBr disks. $^1$H-NMR spectra were measured on a Bruker ARX300 spectrometer (Faellanden, Switzerland) with dimethyl sulfoxide (DMSO) as the solvent. Mass spectrum data were obtained on a JEOL D300 gas chromatograph/

mass spectrometer (Tokyo, Japan). Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co., Harau, Germany). The thermal properties were measured on a PerkinElmer TGA-7 thermogravimetric analyzer (NJ) and a Mettler–Toledo DSC-822e differential scanning calorimeter (Zurich, Switzerland) under a nitrogen atmosphere at a heating rate of 20.0°C/min. The number-average and weight-average molecular weights were determined with a Waters 2410 gel permeation chromatograph (MA) in tetrahydrofuran (THF) with a calibration curve of polystyrene standards. Ultraviolet–visible (UV–vis) and fluorescence spectra were obtained on a Shimadzu UV-265 spectrophotometer (Tokyo, Japan) and Shimadzu RF-540 spectrofluoro-

photometer, respectively. Luminescence spectra were measured with a xenon lamp as the light source. Both excitation and emission bands were set at 5 nm. All the experiments were carried out at 15 ± 1°C.

## Preparation of the monomers and polymer

### 3,6-Diformyl-9-(α-naphthyl)-carbazole (monomer 1)

*Preparation of 9-(α-naphthyl)-carbazole*[19]. A mixture of carbazole (0.05 mol), α-bromonaphthalene (0.054 mol), potassium carbonate (50 mol), copper powder (0.008 mol), and nitrobenzene (100 mL) was put into a three-necked flask equipped with a mechanical stirrer, a dropping funnel, and a Claisen still-head. The reaction mixture was stirred vigorously and heated on an oil bath to gentle reflux. The water produced from the reaction together with some nitrobenzene was distilled from the reaction system. After refluxing for 10 h, the reaction mixture was cooled, and the solvent and the unreacted halides were removed by steam distillation. The residue was filtered, washed, and dried in the air. The crude products were purified by silica gel column chromatography (eluent: ethyl acetate/*n*-hexane = 1 : 10).

Yield: 71%. mp: 123–124°C. IR (KBr pellet, cm$^{-1}$): 3020, 1600, 1580, 1470, 775, 765, 750, 725. $^1$H-NMR (CDCl$_3$, δ): 6.88–8.24 (m, 15H). ANAL. Calcd. for C$_{22}$H$_{15}$N: C, 90.06%; H, 5.16%; N, 4.77%. Found: C, 89.76%; H, 5.03%; N, 4.41%.

*Monomer 1*[20]. N,N-Dimethyl formamide (0.4 mol) was added dropwise to 0.4 mol of phosphorous oxychloride at 0°C. The mixture was left to stand for 1 h at room temperature to complete the formation of the complex reagent. Then, 9-(α-naphthyl)carbazole (0.02 mol) was added to the reaction system. The reaction mixture was heated to the appropriate temperature with stirring for 24 h and poured into broken ice. After neutralization with the base, the mixture was extracted with chloroform and dried with anhydrous magnesium sulfate. The solvent was removed by distillation *in vacuo*, and this gave the solid residue. The crude product was purified by silica gel column chromatography (eluent: ethyl acetate/*n*-hexane = 1 : 3).

Yield: 29%. mp: 189–190°C. IR (KBr pellet, cm$^{-1}$): 3020, 1690, 1580, 1240, 820, 800, 770. $^1$H-NMR (CDCl$_3$, δ): 7.1–8.8 (m, 13H), 10.17 (s, 2H). Mass spectrometry (*m/z*): 349 (M$^+$), 223, 127.

### 2,5-Bis(3-tolylene-triphenylphosphonium bromide)-1,3,4-oxadiazole (monomer 2)

Monomer 2 was prepared according to the previous work.[21]

### Polymer P-OCN

Fresh sodium ethoxide (0.5 mol) was added to a stirring solution of monomers 1 (0.25 mol) and 2 (0.25 mol) in 15 mL of ethanol and 5 mL of chloroform under a nitrogen atmosphere. The reaction mixture was stirred at 0°C for 1 h and at 70°C for 12 h. The solvent was removed under reducing pressure, and the residual was then diluted with dichloromethane and washed with 1N HCl and water. After the organic extract was dried (MgSO$_4$) and concentrated under reducing pressure, a crude polymer product was obtained. Then, the product was dissolved in dichloromethane and precipitated in methanol several times. After filtration and vacuum drying, pale yellow polymer P-OCN was obtained.

Yield: 45%. IR (KBr pellet, cm$^{-1}$): 2924, 2854, 1600, 1498, 1460, 1418, 1074, 804, 696. $^1$H-NMR (DMSO, δ): 7.14–7.89 (m, aromatic and olefinic). ANAL. Calcd. for (C$_{36}$H$_{22}$N$_3$O)$_n$: C, 84.37%; H, 4.30%; N, 8.20%. Found: C, 83.98%; H, 4.33%; N, 7.92%.

## RESULTS AND DISCUSSION

### Synthesis of the polymer

The synthetic approaches to the monomers and polymer are sketched in Scheme 1. Monomer 1 was synthesized by the Vilsmeier reaction in a way similar to that reported by Lee et al.[22] We used a two-step strategy to prepare dialdehyde monomer 1. Additionally, the molar ratio of the Vilsmeier reagent (formed by DMF and POCl$_3$) to 9-(α-naphthyl)carbazole and the reaction temperature had a significant influence on the reaction process. It was found by experimentation that the appropriate ratio of DMF to POCl$_3$ to 9-(α-naphthyl)carbazole was 20 : 20 : 1 (mol/mol) and that the suitable reaction temperature was 140°C. The polymer was synthesized by polycondensation of monomers 1 and 2 via the Wittig reaction. Gel permeation chromatography measurements with polystyrene as the standard indicated that the number-average and weight-average molecular weights of polymer P-OCN were 12,850 and 27,460, respectively. The glass-transition temperature of polymer P-OCN was determined by differential scanning calorimetry to be 110°C.

### UV–vis absorption and fluorescence emission spectra

Figure 1 shows the UV–vis absorption and PL spectra of the polymer in a dilute chloroform solution. The UV–vis absorption spectra showed an absorption peak ($\lambda_{ab}$) around 240 nm attributable to the π–π* transition of the conjugation backbone and a peak around 274 nm assigned to the naphthalene, carbazole, and oxadiazole rings. The PL excitation spectra were overlapped by the absorption spectra and displayed a maximum ($\lambda_{ex,max}$) at 285 nm. In comparing the UV–vis absorption and PL excitation spectra, we found
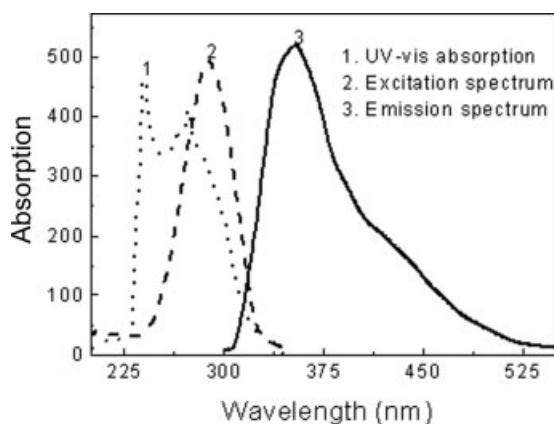
**Figure 1** UV–vis absorption and fluorescence excitation and emission spectra of P-OCN.

that the absorption spectra and fluorescent excitation spectra were obviously different, and this suggested that the excited state of P-OCN (PL excitation) was different from the ground state of P-OCN (the UV–vis absorption). The diversity of spectra could be due to the electron transmission between hole-transporting and electron-transporting moieties of P-OCN in the excited state, which resulted in an extended conjugation range. The polymer emitted blue and blue-green light with an emission maximum ($\lambda_{f,\max}$) at 355 nm in chloroform. Additionally, with the different excited wavelengths, the emission speaks were hardly shifted; however, the emission intensities were obviously changed. This was because the emission spectra of P-OCN strongly depended on the ratio of the carbazole ring (hole-transporting moiety) to the 1,3,4-oxadiazole ring (electron-transporting moiety) in the polymer chain. Research has shown PL emission spectra are obviously redshifted with an increase in the ratio of carbazole and 1,3,4-oxadiazole moieties.[23]

**Solvent effects on PL**

Polymer P-OCN had good solubility in common organic solvents, such as dichloromethane, THF, ethyl acetate, ethanol, acetonitrile, and methanol. The excitation and emission spectra of P-OCN were investigated in different solvents. It can be seen from Figure 2 that the emission spectra of P-OCN were slightly blueshifted with the increase in the solvent polarity. The phenomenon may be due to its structure containing heterocyclic systems, which makes the ($n$–$\pi^*$) excited state more important in P-OCN than the ($\pi$–$\pi^*$) state. The inspected emission peak of P-OCN in solution originated from the transition of the unshared electron pair on the nitrogen atom of 1,3,4-oxadiazole to the $\pi^*$ orbital of the conjugated system. It is well known that solvolytic actions between an unshared electron pair and a polar sol-

vent happen, and this reduces the energy of the $n$ orbital. Thus, more energy will be needed for this transition of an electron from the $n$ orbital to the $\pi^*$ orbital in a solvent with large polarity in comparison with the transition in a solvent with small polarity; this means that the energy gap between $n$ and $\pi^*$ orbitals increases with increasing solvent polarity.[24] Further research toward a better understanding of this effect is currently in progress.

**Quantum yield of the PL and band gap**

The fluorescent quantum yield was measured by a relative method using quinine sulfate as the standard (0.546 in 0.5 mol/L $H_2SO_4$).[25] The quantum yield was calculated with the following equation:

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

where $\Phi$ 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 value of the quantum yield of P-OCN in chloroform was 0.673. The optical band gap ($E_g^{opt}$) of the polymer could be estimated from the onset absorption with $E_g^{opt}$ (eV) = $hc/\lambda$ ($h$ = $6.626 \times 10^{-34}$ J s, $c$ = $3 \times 10^{17}$ nm/s, and 1 eV = $1.602 \times 10^{-19}$ J). It was 3.49 eV.

**Quenching processes of fluorescence of P-OCN with DMA and DMTP**

The fluorescence quenching technique was a helpful method for the study of the mechanism of molecular interaction, energy transfer, or charge transfer. DMA was a typical electron donor, and DMTP was a typical electron acceptor. When DMA was added to a solution of P-OCN in chloroform, the fluorescence of
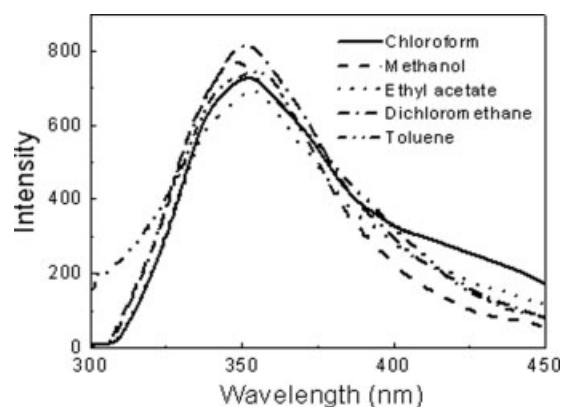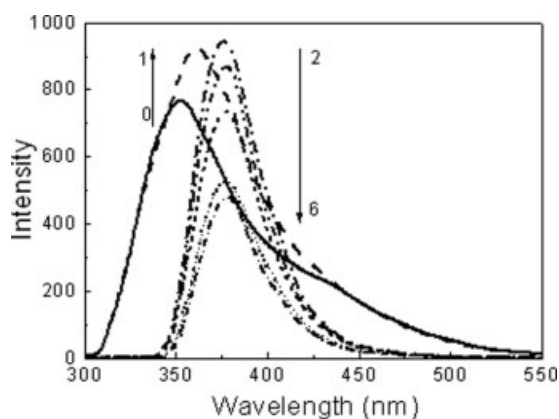


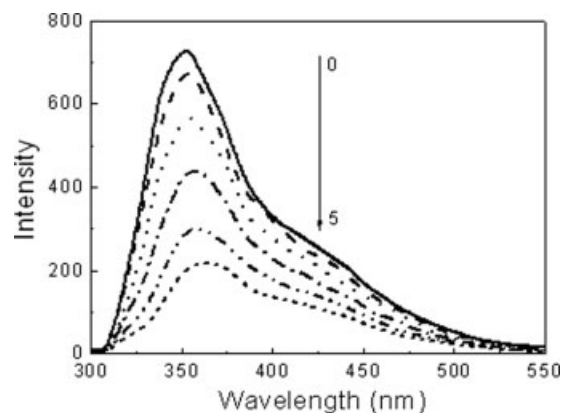**Figure 2** Emission spectra of P-OCN in different solvents.
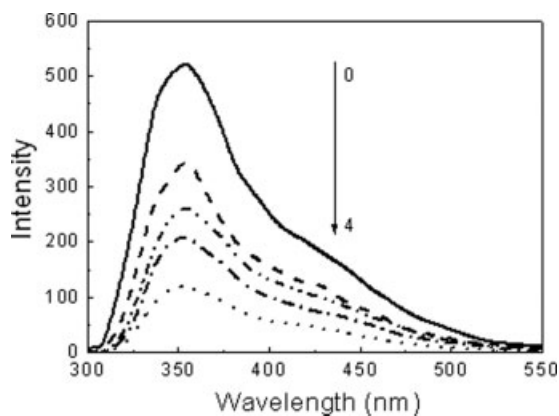
**Figure 3** Fluorescence spectra of P-OCN at different concentrations of DMA. The concentration of P-OCN was $3.43 \times 10^{-3}$ mg/mL; the concentrations of DMA were (0) 0.00, (1) $6.72 \times 10^{-5}$, (2) $1.34 \times 10^{-4}$, (3) $1.61 \times 10^{-4}$, and (4) $2.02 \times 10^{-4}$ mol/L.

P-OCN was efficiently quenched, and the quenching process followed the Stern–Volmer equation. The apparent quenching coefficient was $1.88 \times 10^{4} M^{-1}$ (Fig. 3). The quenching process of P-OCN with DMTP was also examined and is shown in Figure 4. It can be seen that the emission intensity of fluorescence initially increased and then decreased with the concentration of DMTP in chloroform gradually increasing. Meanwhile, the emission peaks redshifted about 30 nm. On the basis of the experimental facts and references, an explanation is proposed: a carbazole unit is an electron-donor group and typical hole-transporting molecule, whereas DMTP is an electron acceptor, so the interaction between the carbazole ring and DMTP happens when DMTP is gradually added to the P-OCN solution. The intramolecular action of the carbazole unit and oxadiazole unit in P-OCN is weakened, and this leads to



**Figure 4** Fluorescence spectra of P-OCN at different concentrations of DMTP. The concentration of P-OCN was $4.42 \times 10^{-3}$ mg/mL; the concentrations of DMTP were (0) 0.00, (1) $1.88 \times 10^{-3}$, (2) $3.76 \times 10^{-3}$, (3) $5.87 \times 10^{-2}$, (4) $6.93 \times 10^{-2}$, (5) $8.22 \times 10^{-2}$, and (6) $9.12 \times 10^{-2}$ mol/L.



**Figure 5** Fluorescence spectra of P-OCN at different concentrations of $C_{60}$. The concentration of P-OCN was $4.42 \times 10^{-3}$ mg/mL; the concentrations of $C_{60}$ were (0) 0.00, (1) $3.52 \times 10^{-7}$, (2) $8.15 \times 10^{-7}$, (3) $1.74 \times 10^{-6}$, (4) $3.13 \times 10^{-6}$, and (5) $4.52 \times 10^{-6}$ mol/L.

increasing fluorescence intensity of the carbazole units. When the concentration of DMTP goes beyond a certain range, the excess DMTP acts as a quencher to quench gradually the fluorescence of P-OCN.

### Interaction between P-OCN and $C_{60}$

Many studies have shown that $C_{60}$ bears many unusual electrochemical and electronic properties. One of the most remarkable properties of $C_{60}$ related to electron-transfer phenomena is that it can efficiently induce rapid charge separation and further slow charge recombination.[26] In the experiment, the interactions of P-OCN with $C_{60}$ were examined. The results are shown in Figure 5. Curve 0 represents P-OCN at a concentration of $4.42 \times 10^{-3}$ mg/mL without $C_{60}$, and curves 1–5 represent P-OCN in the presence of different concentrations of $C_{60}$. With the concentration of $C_{60}$ gradually increasing, the fluorescence of P-OCN was quenched efficiently, and the
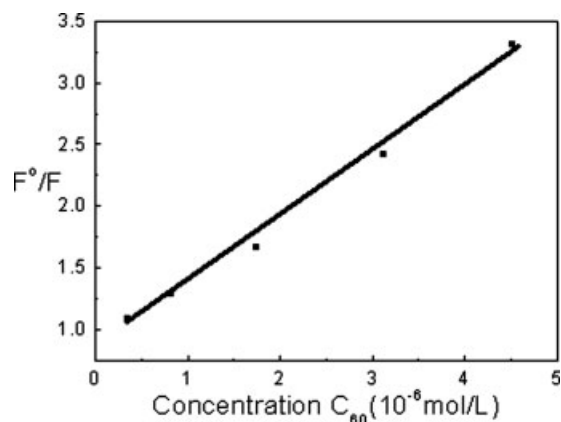


**Figure 6** Dependence of $F^{\circ}/F$ on the concentration of $C_{60}$. The concentration of P-OCN was $4.42 \times 10^{-3}$ mg/mL.

process also followed the Stern–Volmer equation (Fig. 6). The apparent quenching constant was $4.32 \times 10^5 M^{-1}$, which suggests that the strong interactions between P-OCN and $C_{60}$ happened in the excited state. This can be explained in two ways. First, both P-OCN and $C_{60}$ have a large π-conjugated system in which π–π interactions may change the configuration of P-OCN.[27] Second, the photoinduced charge transfer from excited P-OCN to $C_{60}$ was rapid. Upon this charge transfer, the conjugated polymer system may have been dramatically modified and distorted because of the strong electron–lattice interaction in the one-dimensional system.[28]

## CONCLUSIONS

A novel conjugation polymer, P-OCN, containing both electron-transport and hole-transport groups (1,3,4-oxadiazole and carbazole units) in the main chain and fluorophore naphthalene units in the side chain was successfully synthesized by the Wittig reaction. Optical research showed that there were multiple absorptions ranging from 240 to 355 nm and that the emission was located at 355 nm in chloroform. The luminescence quantum yield was 0.673 in chloroform. In addition, the light emission could be quenched by an electron donor, electron acceptor, and $C_{60}$, and the quenched processes followed the Stern–Volmer equation. It can be anticipated that the polymer P-OCN will have potential applications in adjusting the ratio of the injection of electrons and transport of holes in light-emitting diodes used in a wide range.

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