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Synthesis and photoluminescent properties of polymer containing perylene and fluorene units

Liheng Feng, Zhaobin Chen*

School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, People's Republic of China

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Abstract

A new luminescent polymer, F-PTCD, with *N*,*N*′-bis-(propenylaniline)-3,4,9,10-perylene tetracarboxylic diimide-emitting segments (PTCD) and 9,9-diphenylfluorene (DIPT) was synthesized by Heck reaction. The structures were characterized by MS, EA, ^{1}H NMR, IR and the photoluminescent (PL) properties were investigated by UV/vis absorption and fluorescence emission spectra. The fluorescence quantum yield was 0.453 in acetone. Thermogravimetric analysis and differential scanning calorimetry showed that the polymer is thermal stable up to 569 °C with glass-transition temperature higher than 125 °C. They are yellow–red emitting materials with the band gap of 2.33 eV estimated from the onset absorption. In addition, the emission can be quenched by both electron donor (*N*,*N*-dimethylaniline) and electron acceptor (Fullerene), where the processes followed the Stern-Volmer equation. Furthermore, the interaction between F-PTCD and carbon nanotubes (CNTs) was also studied by fluorescent quenching.

Keywords: *N*,*N*′-Bis-(propenylaniline)-3,4,9,10-perylene; Tetracarboxylic diimide; Heck reaction

1. Introduction

The field of research into polymers is growing rapidly due to the versatility and potential applications of these materials. It is well known that a good luminescent material should possess high photoluminescent efficiency, excellent charge transport ability and film-forming property [1–3]. Perylene-based polymers are of broad interest owing to their wide range of potential applications including electron-transporting components in organic light-emitting diodes [4], semiconducting materials for electrophotography [5], photovoltaic materials for solar energy conversion [6], photorefractive materials for optical signal processing [7] etc. Fluorene derivatives show unique photoelectric properties in that they contain a rigid planar biphenyl unit and facilely initiate a substitution at C_9 position of fluorene, which will improve the solubility and processability of polymers containing fluorene without significantly increasing of steric interactions in the polymer backbone [8]. As a result, polymers based on fluorene have emerged as high efficient and thermal stable materials [9–11]. Derivatization of perylene with highly fluorescent fluorene derivatives in polymer molecules [12] leads to considerable advantages of photophysical and photochemical properties. Therefore, the synthesis and spectroscopic investigation of such polymer are of considerable interest.

In this work, a novel polymer containing of 9,9-diphenylfluorene (DIPF) moieties and *N*,*N*′-bis(propenylaniline)-3,4,9,10-perylene tetracarboxylic diimide (PTCD) moieties was synthesized and characterized. We present the photoluminescence (PL) studies of F-PTCD with particular emphasis on the molecular interactions of F-PTCD with *N*,*N*-dimethylaniline (DMA), fullerene (C_{60}) and carbon nanotubes (CNTs). Perylene diimide molecules, compared with the parent perylene, their absorption maximum red-shifted to a long wavelength region with an increase in the extinction coefficients up to. The position of λ_{max} is not very sensitive to the structure of N-substituents and a small spectral shift with different substituents suggests the π–π transitions of perylene diimide are localized in the perylene ring. Polymer F-PTCD combines the perylene ring system with a fluorene derivative. The combination is expected to

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* Corresponding author. Tel.: +86 351 701 1492; fax: +86 351 701 1688.

E-mail address: zchen@sxu.edu.cn (Z. Chen).

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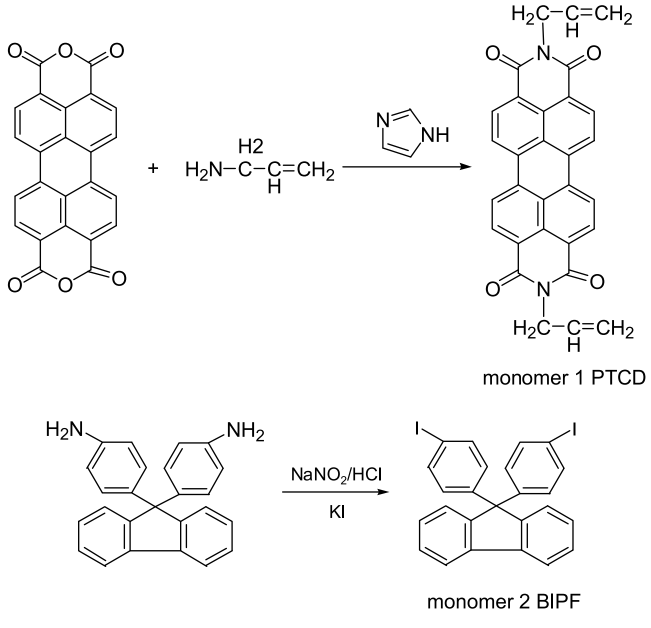
expand the variety of photophysical and photochemical properties of perylene-based organic dyes and the luminescent materials. The relatively elongated molecular geometry of F-PTCD suggests that it may exhibit a high value of fluorescence probes.

2. Experimental

2.1. Materials and instruments

The reagents and chemicals for preparation of monomers and polymer were used as received unless noted otherwise. Ethanol, acetonitrile, acetone, THF, DMSO, ethyl acetate, petroleum ether were purchased from Beijing Chemical Plant and treated according to standard methods used before, which were 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 uncorrected. The IR spectra were determined on a PE-1700 IR spectrophotometer by dispersing samples in KBr disks. ^{1}H NMR spectra were measured on a Bruker ARX300 spectrometer with DMSO as a solvent. Mass spectroscopy dates were obtained on a JEOL GC-MS D300. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.) The thermal properties were measured on a PerkinElmer TGA-7 thermogravimetric analyzer, and a Mettler-Toledo DSC-822e differential scanning calorimetry (DSC) under nitrogen atmosphere at a heating rate of 20.0 °C/min. Number-average (M_n) and weight-average (M_w) molecular weights were determined by a waters GPC 2410 in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. UV–Visible and fluorescence spectra were obtained on a Shimadzu UV-265 spectrophotometer and Shimadzu RF-540 spectrofluorothotometer, respectively. Luminescence spectrometer was with a xenon lamp as the light source. Both excitation and emission bands were set at 10 nm. All the experiments were carried out at 20 ± 1 °C.



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

2.2. Synthesis of monomers (Scheme 1)

2.2.1. N,N′-bis-(propenylaniline)-3,4,9,10-perylene tetracarboxylic diimide (PTCD)

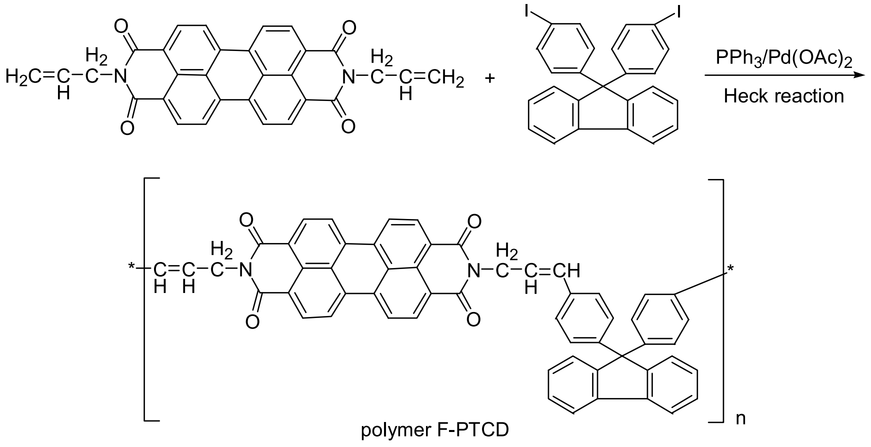
PTCD was synthesized according to the literature [13]. The mixture of 3,4,9,10-perylenetrtracarboxylic dianhydride (1.0 g, 2.55 mmol), allylamine hydrochloride (10.2 g, 109.1 mmol) and imidazole (5.0 g, 73.3 mmol) was heated at 160 under nitrogen atmosphere for 4 h. The ethanol (100 ml) was added to the reaction solution, and the ethanol solution was acidified by addition of the hydrochloric acid (2 mol/l, 300 ml) to give PTCD in 58% yield, mp > 350 °C. IR (KBr, cm^{-1}): 3050, 2925, 2850, 1695, 1660, 1590, 1575, 1530, 1470, 1430, 1370, 1345, 1310, 1300, 1270, 1170, 1125, 1002, 988, 915, 899, 850, 810, 795, 750. IR is identical with that described in literature. ^{1}H NMR (DMSO, ppm) δ: 8.01–7.56 (8H, aromatic), 5.45 (6H, CH=CH$_2$), 3.96 (4H, 2-N–CH$_2$). Element Anal. Calcd for $C_{30}H_{18}N_2O_4$: C, 72.29; H, 3.61; N, 11.24. Found: C, 72.51; H, 3.66; N, 11.36.

2.2.2. 9,9-Bis(4′-iodophenyl)fluorene (BIPF) monomer [14]

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 cooled 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, 5.0 mmol) and potassium iodide (0.664 g, 4.0 mmol) in water (50 ml) was poured into the reaction mixtures and heated under stirring until no bubble generating. The precipitates were appeared after adding 40 ml water and was then dissolved in ethanol. After the precipitates were filtered off. The remained liquid was poured into water, giving a white solid. The pure product, 9,9-bis(4′-iodophenyl)fluorene (BIPF) was given in 81.5% yield after recrystallization from anhydrous ethanol, mp: 183–184 °C. MS (EI, *m/z*): 570 (M$^+$); ^{1}H NMR (DMSO, ppm) δ: 7.72–7.35 (16H, aromatic). IR (KBr, cm^{-1}): 1601, 1575, 1483, 1446 (⌬), 802 (–⌬–), 484 (C-I). Element Anal. Calcd for $C_{25}H_{16}I_2$: C, 52.65; H, 2.81. Found: C, 52.54; H, 2.88.

2.2.3. Synthesis of polymer F-PTCD [15] (Scheme 2)

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 *N,N′*-bis-(propenylaniline)-3,4,9,10-perylene tetracarboxylic diimide (1.175 g, 2.5 mmol) were dissolved in 300 ml dry DMF and stirred



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

at 140 °C under nitrogen atmosphere for 48 h. Water (200 ml) was added, and the precipitate was collected by filtration. The purple black 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 (1:2) as the eluant to give in 20.4% yield violet red solids. ^{1}H NMR (DMSO, ppm) δ: 7.83–7.27 (28H, aromatic), 4.15 (4H, 2-N–CH_2). IR (KBr, cm^{-1}): 3062 (C=C–H), 1687, 1692 (C=O), 1602 (C=C), 1595, 1541, 1505, 1436 (⌬). Element Anal. Calcd for F-PTCD: C, 81.28; H, 3.94; N, 6.89. Found: C, 81.21; H, 3.89; N, 6.92; $M_w = 33{,}000$, $M_n = 14300$.

3. Results and discussion

3.1. Synthesis and characterization

The polymer (F-PTCD) was synthesized by Heck reaction of 9,9-bis(4′-iodophenyl)fluorene with *N*,*N*′-bis-(propenylaniline)-3,4,9,10-perylene tetracarboxylic diimide. Although this is a well-estabilished method for C–C bond formation, but 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 $Pd(OAc)_2$ to $P(Ph)_3$ is 1:4 (mol), which can successfully form the reactive catalyst. The suitable reaction temperature 140 °C.

The IR spectra of monomer BIPF show the disappearance of 3414, 3397 cm^{-1} (–NH_2) and the appearance of 484 cm^{-1} (Ar–I), which indicate the BIPF is successfully synthesized. The IR spectra of polymer F-PTCD show the sharp peak 1687 and 1629 cm^{-1}, which corresponds to the carbonyl group of amide. In the IR spectra of the polymer the peak at 484 cm^{-1} disappear completely. These results indicate the polymer was successfully formed. The thermal properties of polymer were examined with DSC and TGA analysis. The glass transition temperature was higher than 125 °C. Moreover, it exhibits good thermal stability for the weight loss was less 17% on heating up to 569 °C.

3.2. UV–vis absorption and fluorescence emission spectrum

The UV–vis absorbance spectra of PTCD and F-PTCD are showed in Fig. 1 From the chemical structure of F-PTCD, It consists of chromophore system: a perylene diimide and fluorenyl groups. The spectral properties of perylene diimide are not very sensitive to the structure of fluorenyl groups. In contrast, the combination of the fluorenyl group with perylene diimide results in a blue shift of the position of λ_{max} of the fluroneyl moiety, owing to the electron-withdrawing nature of the diimide. The absorption spectrum of the PTCD show three peaks at 342, 463 and 513 nm. The absorption peaks of the F-PTCD are located at 334, 447 and 500 nm. Fig. 2 shows the photoluminescence spectra (PL) of the solution of PTCD and F-PTCD in acetone. The emission spectrum of the PTCD show three peaks at 355, 442 and 531 nm, whereas the emission spectrum of the F-PTCD are located at 390, 475 and 532 nm. By comparison with PTCD, the emission spectra of F-PTCD show slightly red-shift. These

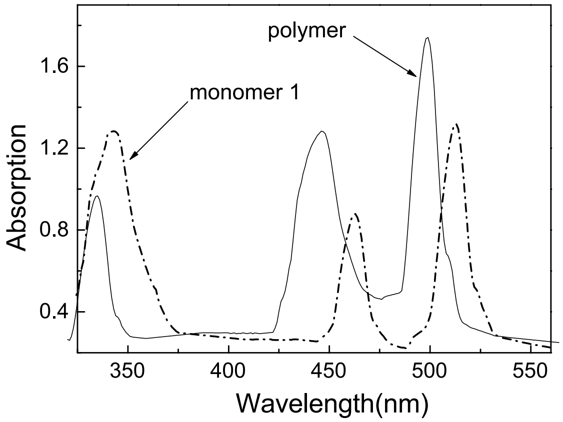


Fig. 1. UV–vis absorption spectra F-PTCD and PTCD in acetone.

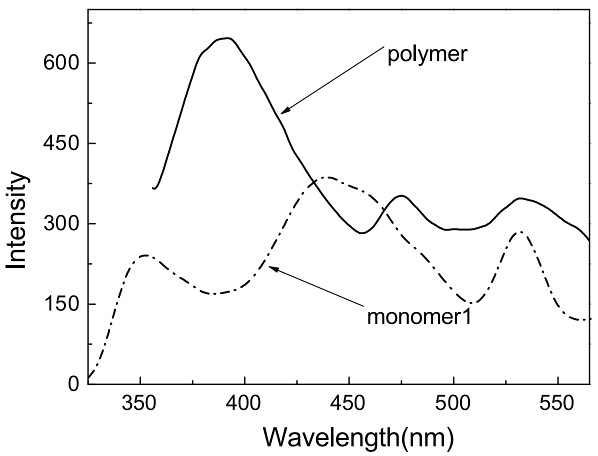


Fig. 2. Fluorescent emission spectra of F-PTCD and PTCD in acetone.

phenomena can be attributed to their different configuration, greater π system in F-PTCD than that in PTCD.

3.3. Quantum yield of photoluminescence and the band gap

The fluorescence quantum yield was measured by relative method using the quinine sulfate as the standard (0.546 in 0.5 mol l^{-1} H_2SO_4) [16]. The quantum yield was calculated from the following equation:

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

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 value of quantum yield of F-PTCD in acetone is 0.453. The band gap (E_g^{opt}) of the polymer can be estimated from the onset absorption (UV_{onset}) with E_g^{opt} (eV)$=hc/\lambda$ ($h=6.626\times10^{-34}$ J s, $c=3\times10^{17}$nm/s, 1 eV$=1.602\times10^{-19}$ J). The band gap of the polymer is 2.33 eV.

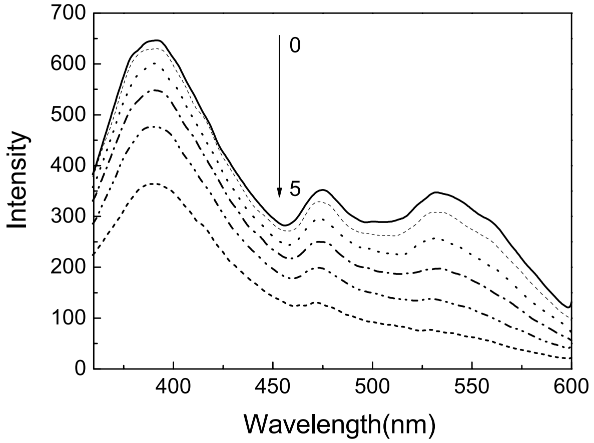


Fig. 3. Fluorescence spectra of F-PTCD at different concentration of DMA. Concentration of F-PTCD 0.98×10^{-2} mg/ml. Concentration of DMA (mol/l, M), 0, 0.00; 1, 8.06×10^{-5}; 2, 2.32×10^{-4}; 3, 4.53×10^{-4}; 4, 9.57×10^{-4}; 5, 1.76×10^{-3}.

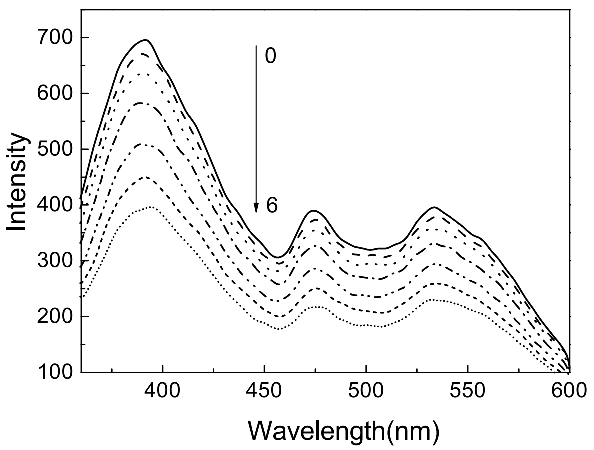


Fig. 4. Fluorescence spectra of F-PTCD at different concentration of C60. Concentration of F-PTCD, 1.05×10^{-7} mg/ml. Concentration of C60 (mol/l, M), 0, 0.00; 1, 1.85×10^{-7}; 2, 6.49×10^{-7}; 3, 1.58×10^{-6}; 4, 2.96×10^{-6}; 5, 4.82×10^{-6}; 6, 7.14×10^{-6}.

3.4. The quenching process of fluorescence of F-PTCD with N,N-dimethylaniline (DMA)

The fluorescence quenching technique is an effective method for study of the mechanism of molecular interaction. *N*,*N*-dimethylaniline (DMA) is a typical electron donor, so the studies of interactions between F-PTCD and DMA are helpful to understand the optical electronic properties of F-PTCD. Fig. 3 shows the emission spectra of F-PTCD in acetone with different concentrations of DMA. From the Fig. 3, we can see that the fluorescence of F-PTCD 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 4.56×10^2 M^{-1}.

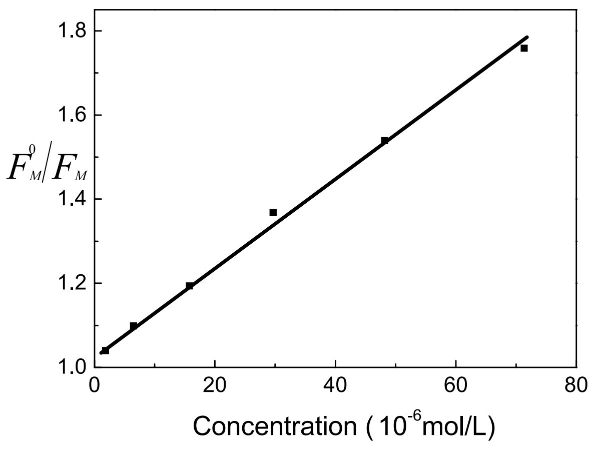


Fig. 5. Dependence of *F F M M* 0 on concentration of C_{60}. Concentration of F-PTCD 1.05×10^{-2} mg/ml.

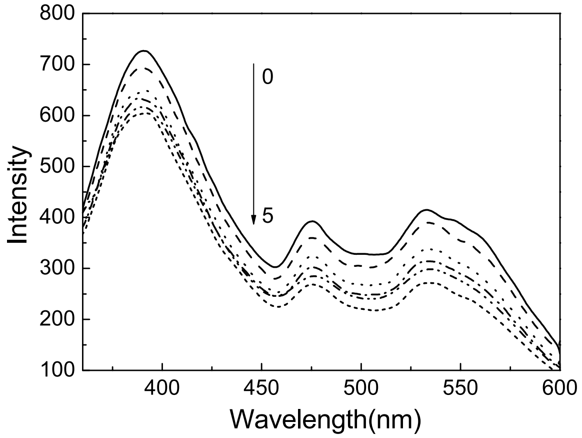


Fig. 6. Fluorescence spectra of F-PTCD at different concentration of CNTs. Concentration of F-PTCD, 1.12×10^{-2} mg/ml; concentration of CNTs (mg/ml), 0, 0.00; 1, 4.22×10^{-7}; 2, 8.44×10^{-7}; 3, 9.27×10^{-6}; 4, 3.75×10^{-5}; 5, 5.83×10^{-5}.

3.5. Interaction between F-PTCD and fullerene (C_{60})

Many investigations show that C_{60} is a good electron acceptor. It possesses a wide range of physical and chemical properties. One of the most remarkable properties of C_{60} is to induce efficiently a rapid charge separation and a further slow charge recombination [17]. In the experiment, the interactions of F-PTCD with C_{60} are examined and the results are shown in Fig. 4. As we have seen in Fig. 4, ‘0’ is F-PTCD in concentration (1.05×10^{-2} mg/ml) without C_{60}, ‘1–6’ are F-PTCD in the present in different concentration of C_{60}. With the gradual increasing of concentration of C_{60}, the fluorescence of F-PTCD is quenched efficiently and the process is also following the Stern–Volmer equation (Fig. 5). The apparent quenching constant is $1.06\times10^{5}\ \mathrm{M}^{-1}$, which suggests that the strong interactions between F-PTCD and C_{60} happen in the excited state. The interactions are mainly coming from the stronger charge-transfer process of the long π electron system (F-PTCD) with the electron acceptor (C_{60}).

3.6. Interaction between F-PTCD and carbon nanotubes (CNTs)

Carbon nanotubes are unique tubular structures of nanometer diameter and have large length/diameter ratio [18]. It shows promise for a wide range of applications due to a combination of their unusual structural, mechanical and electronic properties [19]. The investigation on the interaction between F-PTCD and carbon nanotubes (CNTs) is helpful to understand the optical property of F-PTCD and apply it to LEDs. The quenching process of F-PTCD with carbon nanobutes is shown in Fig. 6. It can be seen that the fluorescence of F-PTCD is quenched. Similarly, the strong interacting between F-PTCD and CNTs are initiated in the excited state. The strong interaction may be caused by the photoinduced charge transfer and stacking processes of initiated π–π system.

4. Conclusions

We successfully prepared and characterized a novel polymer F-PTCD containing *N*,*N*′-bis-(propenylaniline)-3,4,9,10-perylene tetracarboxylic diimide-emitting segments and 9,9-diphenylfluorene segments. The absorption and photoluminescence maximum of the polymer are at around 500 and 532 nm, respectively. The quantum yield of photoluminescence was 0.453 and the polymer was stable beyond 569 °C. Furthermore, the interactions between F-PTCD and fullerene or carbon nanobutes were investigated. The result indicates that the strong interactions are to appear between F-PTCD and C_{60} or CNTs at the exited states.

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