Synthesis, characterization, electrochemistry and optical properties of a novel phenanthrenequinone-alt-dialkylfluorene conjugated copolymer

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Abstract: This paper describes the synthesis, characterization and electro-optical properties of a 9,10-phenanthrenequinone (PQ)-containing alternating conjugated copolymer: poly[(9,10-phenanthrenequinone-2,7-diyl)-alt-(9,9-di-n-hexylfluorene-2,7-diyl)] (PPQF). The copolymer has good solubility in common organic solvents such as CH2Cl2, CHCl3 and tetrahydrofuran. The polymer structure was determined using 1H NMR, Fourier transform infrared spectroscopy, gel permeation chromatography and elemental analysis. The polymer possesses a low-energy \( n \rightarrow \pi^* \) electronic state caused by the C=O groups of the PQ repeating units, and exhibits interesting and improved electrochemical reduction activity as compared to poly(9,9-di-n-hexylfluorene-2,7-diyl) and molecular PQ. PPQF has no fluorescence in solution but shows interesting transitions from no fluorescence to strong fluorescence after it undergoes electrochemical reduction. The polymer PPQF may find use as a starting material for a range of applications and can also be used to prepare other polymers due to the presence of the PQ repeating units.

Keywords: 9,10-phenanthrenequinone; holography; electrochemical sensors; conjugated polymers; reduction; fluorescence

INTRODUCTION

Conjugated polymers are an important class of materials because of their unique optical and electrical properties. The synthesis and the photo-physical properties of polymers containing carbonyl groups are of great interest because of their physical and chemical versatility. 9,10-Phenanthrenequinone (PQ; Scheme 1) is an important photo-acid in its excited state in hydroxylated solvents and a crucial reduction-active 1,2-diketone that has been widely studied in the fields of holography, oxidized semiconductor Si(001) surfaces, electrochemical sensors, chemically modified electrodes, pharmaceutical chemistry and biochemistry. In electrochemical reduction, the carbonyl groups of PQ can undergo reversible one- and two-electron reduction processes to produce semiquinone radical species, which are responsible for the bioactivity of PQ-containing enzymes. PQ is a photosensitive molecule, which can react via photoinduced electron transfer under visible light irradiation.

Based on the concept of ‘conjugated molecular wire’ established by Swager and co-workers, electron and energy migration can occur along the conjugated polymer backbone upon excitation due to the conductivity of the backbone; thus enhanced photo- and electrochemical activities are prefigured, as one incorporates PQ into a \( \pi \)-conjugated system. Polyfluorene-based conjugated polymers (PFs) are processable materials of much interest possessing good solubility in common organic solvents, which have received considerable attention for their high solid-state efficiency, both in photoluminescence (PL) and electroluminescence (EL) as well as their good charge transport properties. Due to their pure blue and efficient EL coupled with a high charge carrier mobility and processability, they have been considered for display applications. PFs also possess excellent thermal stability and high stability against oxidants.

Considering the properties of PFs and PQ and recent advances in fluorene polymers, a copolymer containing both units, poly[(9,10-phenanthrenequinone-2,7-diyl)-alt-(9,9-di-n-hexylfluorene-2,7-diyl)] (PPQF), can be very useful for a broad range of applications as discussed above. We have studied the characteristics of the polymer structure and its electrochemical properties. The active sites of PQ are the two ortho-carbonyl groups present in each repeating unit of PPQF. These sites provide
a very unique opportunity for modification and hence make this material potentially valuable for applications in semiconductors and volume storage devices. With the aiming of improving the activity of the PQ receptor and extending its applications, the PQ–fluorene alternating copolymer PPQF was synthesized and characterized. This is the first description of a conjugated polymer containing PQ in its backbone. The PPQF copolymer shows interesting reduction activity and optical properties in subsequent electrochemical reduction procedures. Herein, we report the results.

EXPERIMENTAL

Measurements

Melting temperatures were determined using an IA 6304 electrothermal melting point apparatus and are uncorrected. ¹H NMR spectra were recorded using a Bruker AVANCZ 500 spectrometer at 500 MHz, with DMSO-d₆ or CDCl₃ as solvent at 298 K and tetramethylsilane (TMS) as the internal standard. Fourier transform infrared (FTIR) spectra in KBr pellets were obtained using a Bruker IFS66V FT-IR spectrometer. Number-average (Mn) and weight-average (Mw) molecular weights were determined by gel permeation chromatography (GPC) with an HPLC Waters 510 pump using a series of low-polydispersity polystyrene standards using tetrahydrofuran (THF; HPLC grade, Aldrich) as eluent at 308 K. UV-visible absorption spectra were recorded with a Hewlett-Packard diode-array spectrophotometer (model 8452A) using 1 cm path length quartz cells. Electrochemical measurements were performed with a BAS 100W bioanalytical system. For voltammetry procedures the solvents and electrolytes were added to a cell containing working, reference and counter electrodes protected under nitrogen. The solution was degassed with nitrogen for 2 min. After recording a background scan, the quinone and internal reference, if needed, were added for solution-phase experiments and the cyclic voltammogram was obtained.

Materials

Fluorene, PQ, 1-bromohexane, n-butyllithium (2.5 mol L⁻¹ in hexane), FeCl₃, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, N-bromosuccinimide (NBS) and [(PPh₃)₄]Pd(0) were purchased from Aldrich and used without further purification. THF and diethyl ether were dried and purified by fractional distillation over sodium in the presence of benzophenone. All other chemicals were purchased from Acros and used without further purification.

Synthesis of monomers and polymers

The monomers M2, M4, M5, M6 (Scheme 2), and the polymers PPQF and poly(9,9-di-n-hexylfluorene-2,7-diyl) (PDHF) were synthesized according to reported procedures.³⁷,³⁸

![Scheme 1](image1)

Scheme 1. Chemical structures of (1) 9,10-phenanthrenequinone (PQ), (2) poly(9,9-di-n-hexylfluorene-2,7-diyl) (PDHF) and (3) poly[(9,10-phenanthrenequinone-2,7-diyl)-alt-(9,9-di-n-hexylfluorene-2,7-diyl)] (PPQF).

![Scheme 2](image2)

Scheme 2. Synthetic routes to the monomers. The reagents and conditions are as follows: (i) NBS, room temperature; 98% H₂SO₄, 2 h, room temperature; (ii) 2 eq. n-BuLi (2.5 mol L⁻¹ in hexane), −78 °C, THF, 45 min; (iii) C₆H₁₃Br dropwise, at −78 °C for 1 h, stirring at room temperature for 3 h; (iv) 2 eq. Br₂ (liq.), CHCl₃, 0 °C, (v) FeCl₃ (2 mol%) in CHCl₃, 24 h, 25 °C; (vi) 2.1 eq. n-BuLi, THF, −78 °C, 1 h; (vii) 2.5 Eq. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, room temperature, 24 h.
Polymerization procedure of PPQF (Scheme 3)

In a 25 mL round-bottom flask, 2,7-dibromo-9,10-phenanthrenequinone (DBPQ, M2; 1 mmol, 366.0 mg), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-n-hexylfluorene (1 mmol, 586.4 mg) and [(PPh3)4]Pd(0) (2 mol%, 46.2 mg) were placed. Toluene (5 mL) and aqueous 2 mol L\(^{-1}\) Na\(_2\)CO\(_3\) (2 mL) were then added. The mixture was first put under a nitrogen atmosphere and was refluxed with vigorous stirring for 72 h. The whole mixture was then poured into 150 mL methanol; the precipitated material was recovered by filtration through a Buchner funnel and washed with dilute HCl. The solid material so obtained was washed for 24 h in a Soxhlet apparatus using acetone to remove oligomers and catalyst residues. The resulting solid, 405.5 mg (75% yield), was polymer PPQF, soluble in CH\(_2\)Cl\(_2\), THF and CHCl\(_3\). 1H NMR (CDCl\(_3\), ppm): \(\delta = 8.56\) (m, 2H, PQ–Ar–H), 8.17 (brs, 2H, PQ–Ar–H), 7.87 (m, 2H, Fluo–Ar–H), 7.70 (m, 4H, Fluo–Ar–H), 2.13 (m, 4H, Fluo–Alk–CH\(_2\)), 1.12 (m, 12H, Fluo–Alk–CH\(_2\)). FTIR (KBr pellets, cm\(^{-1}\)): 3033 (\(\nu =\) C–H, arom. stretch), 2954, 2924, 2850 (2\(\nu\) C–H aliph. stretch), 1681 (C=O stretch of PQ), 1597 (C=C arom. stretch), 1461 (C=C arom. stretch), 1353, 1250, 1144, 815 (OOPC–H bend of 1,2,4-substituted phenyls), 717. \(M_w = 20545\), \(M_n = 12085\); polydispersity (PDI) = 1.7 (by GPC). Analysis. Calc. (for C\(_{39}\)H\(_{38}\)O\(_2\)): C, 86.95; H, 7.11; O, 5.94. Found: C, 84.50; H, 7.38; O, 6.06.

RESULTS AND DISCUSSION

Synthesis and structural characterization

Scheme 2 shows how the monomers were prepared using PQ (M1) and fluorene (M3) as starting materials. For the synthesis of DBPQ monomer (M2), concentrated 98% H\(_2\)SO\(_4\) was added to a mixture of NBS and PQ, which was stirred at room temperature for 2 h. Slow addition of water to the reaction flask with stirring for an hour destroyed succinimide (a by-product) by converting it to water-soluble succinic acid which was washed away during filtration. The concentration of H\(_2\)SO\(_4\) also plays an important role as dilute H\(_2\)SO\(_4\) can lead to a mixture of products that are difficult to separate. Dimethylsulfoxide (DMSO) was found to be the appropriate solvent for recrystallization of DBPQ.

The synthesis of boronic ester monomer (M6) was accomplished, using fluorene (M3) as starting material, according to a reported procedure.\(^{38}\) The Pd(0)-catalyzed Suzuki coupling reaction (Scheme 3) between M2 (DBPQ) and diboronic ester (M6) was performed in the presence of 2 mol% of [(PPh\(_3\))\(_4\)]Pd(0) catalyst in a mixture of toluene and water, for 72 h. The resulting mixture was precipitated into methanol and collected by filtration. The solid obtained was washed with cold methanol and dilute HCl to remove impurities. Use of a Soxhlet apparatus and acetone as solvent for 80 h under nitrogen atmosphere to remove oligomers and catalyst residues allowed the purification of the polymer PPQF.

It should be pointed out that the Yamamoto coupling reaction for the preparation of the copolymer inevitably incorporates oligomeric segments into the polymer chains. In contrast the polymerization using the Suzuki coupling reaction\(^{39}\) produces well-defined alternating molecular structure, thus ensuring the incorporation of PQ in the desired copolymer very close to the monomer feed ratio (1:1), which could be confirmed by \(^1\)H NMR. In addition, a review of the Suzuki coupling reaction\(^{39}\) shows that this reaction has not been applied to ortho-diketones so that polymer PPQF presents a new example of the Suzuki coupling reaction and an example of mild reaction conditions.\(^{40}–42\)

Because of the use of carefully purified DBPQ and boronic ester of fluorene, one is unlikely to obtain homopolymer. This synthetic procedure can only give alternating PPQF due to the mildness of the Suzuki reaction. It is clear that PPQF can show amphiphilic properties\(^{40}\) as each repeating unit has one dihexylfluorene unit, which has a hydrophobic nature while PQ exhibits hydrophilic properties. These interesting properties are particularly useful for the preparation of well-defined Langmuir–Blodgett films.\(^{43,44}\) This alternating copolymer can be useful for the preparation of well-defined and processable new alternating π-conjugated polymers due to the presence of ortho-carbonyl groups.
### Table 1. Comparison between physical properties of PDHF and PPQF

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Color(^a)</th>
<th>(M_n)(^b)</th>
<th>(M_w)(^b)</th>
<th>PDI, (M_w/M_n)</th>
<th>Absorption (\lambda_{\text{max}}) (nm), THF solution</th>
<th>Emission (\lambda_{\text{max}}) (nm), THF solution</th>
<th>(\Phi)(^d) in THF solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDHF</td>
<td>White</td>
<td>24 300</td>
<td>34 500</td>
<td>1.4</td>
<td>380 (439)(^c)</td>
<td>415 (438)(^c)</td>
<td>0.79</td>
</tr>
<tr>
<td>PPQF</td>
<td>Red</td>
<td>12 085</td>
<td>20 545</td>
<td>1.7</td>
<td>370 (465)(^c)</td>
<td>417 (438)(^c)</td>
<td>0.07</td>
</tr>
</tbody>
</table>

\(^a\) Color under visible light.
\(^b\) From GPC with polystyrene as internal standard, using THF as eluent.
\(^c\) The data in parentheses are the wavelengths of sub-peaks.
\(^d\) PL quantum yield with respect to quinine sulfate in 0.10 mol L\(^{-1}\) H\(_2\)SO\(_4\).

Figure 1. \(^1\)H NMR (CDCl\(_3\)) spectrum of polymer PPQF.

On the basis of GPC using THF as the eluent and polystyrene as the internal standard, this versatile synthesis provided PPQF with satisfactory molecular weights (Table 1). The weight-average and number-average molecular weights of PPQF are 20 545 and 12 085 g mol\(^{-1}\), respectively. The polydispersity index \((M_w/M_n)\) is 1.7, which is consistent with a polycondensation reaction and shows the theoretical molecular weight distribution. In the structure of PPQF, the polyfluorene backbone provides rigid planarity, the side chain hexyl groups at C-9 of fluorene provide good solubility to make the polymer processable and the two active ortho-carbonyl groups of PQ are favorable for physical and chemical modification.

\(^1\)H NMR analysis of the copolymer PPQF (Fig. 1) clearly indicates that well-defined PPQF has been obtained. From \(^1\)H NMR data of DBPQ (Fig. 2) we can identify three peaks between 8.26 and 7.95 ppm corresponding to the three aromatic protons of DBPQ. Three similar peaks at 8.56, 8.17 and 8.08 ppm, respectively, are observed in the \(^1\)H NMR spectrum of PPQF. The \(^1\)H NMR spectrum of PPQF also has peaks between 7.87 and 7.70 ppm, corresponding to the well-known aromatic protons of the fluorene unit. Peaks at 2.13, 1.12 and 0.77 ppm are attributable to the protons of dihexyl chains attached to the fluorene unit in PPQF. The other peaks in this region are solvent peaks. It is evident from Fig. 1 that the PPQF structure is consistent.

FTIR analysis\(^{46,47}\) (Fig. 3) of PPQF indicates the aromatic phenyl hydrogen stretch (=C–H) at 3033 cm\(^{-1}\) for the backbone. The strong aliphatic C–H stretches at 2954, 2924 and 2850 cm\(^{-1}\) are attributed to the flexible hexyl chains of the fluorene unit in PPQF. The prominent peak at 1681 cm\(^{-1}\) is attributed to the two C=O groups of PPQF. This value is well known for conjugated C=O groups and gives strong evidence for the presence of PQ units in the polymer backbone. The peaks at 1597 and 1456 cm\(^{-1}\) belong to the aromatic C=C stretch and show the presence of aromatic rings in the polymer chain. The intense sharp peak for the out-of-plane (OOP) bending vibrations at about 815 cm\(^{-1}\) corresponds to the 1,2,4-substituted phenyl rings of the backbone of PPQF.

### Fluorescence properties

The absorption and PL spectra of polymers PPQF and PDHF in THF solutions (Fig. 4) were measured at room temperature. The results of the absorption, PL emission and other physical properties are summarized in Table 1. Copolymer PPQF shows absorption peaks (Table 1 and Fig. 4) at \(\lambda_{\text{max}} = 370\) nm (3.35 eV).
Figure 4. UV-visible absorption and PL emission spectra of PPQF and PDHF in dilute THF solution. In both cases the concentration is about 1 x 10⁻⁵ mol L⁻¹ in order to avoid inner filter effects.

corresponding to the \( \pi \rightarrow \pi^* \) transition of the aromatic units of the polymer backbone and \( \lambda_{\text{max}} = 465 \text{ nm} \) (2.66 eV) which corresponds to the \( n \rightarrow \pi^* \) transitions of the C=O group of the PQ units. The copolymer shows PL emission at 417 nm with a sub-peak at 438 nm in the blue region, very similar to the emission of PDHF. Unlike polyfluorene (PDHF), which is colorless with an absorption peak at \( \lambda_{\text{max}} = 380 \text{ nm} \) in THF solution under visible light and gives strong blue fluorescence under a UV lamp (PL quantum yield \( \Phi_t = 0.79 \), THF solution), PPQF exhibits a bright red color in solution under visible light and no fluorescence (\( \Phi_t = 0.07 \), THF solution) under a UV lamp. The bright red color of PPQF is due to the presence of a low-energy band in the absorption spectra that extends up to 600 nm (Fig. 4). This low-energy band originates from the unfavorable orientation of non-bonding electrons of oxygen of the C=O group relative to the \( \pi^* \) anti-bonding orbital. In addition, the low-energy absorption band (\( \lambda_{\text{max}} = 465 \text{ nm}, \epsilon = 4920 \text{ L mol}^{-1} \text{ cm}^{-1} \)) in PPQF is assigned to the \( n \rightarrow \pi^* \) transition of PQ repeating units in the polymer backbone, as PQ monomer alone also shows similar absorption features (\( \lambda_{\text{max}} = 412 \text{ nm} \) and \( \lambda_{\text{max}} = 501 \text{ nm} \)).

The difference in the absorption \( \lambda_{\text{max}} \) values of PPQF and PDHF is small (10 nm) which indicates that there is no interruption in the \( \pi \)-conjugation of the dihexylfluorene and the PQ units. The small blue shift of 10 nm in the absorption spectrum of PPQF relative to PDHF is presumably due to the lower molecular weights (Table 1) of PPQF. The lower \( M_n \) and \( M_w \) values reflect the lower degree of polymerization and shorter conjugation length. However, shorter conjugation chain length does not affect the PL emission \( \lambda_{\text{max}} \) values of PPQF very much, so the THF solution PL spectra of the two polymers are very similar. It is likely that the energy difference in the PL spectra of the two polymers stems from the chain length and the presence of an angle between the planes of the two C=O groups.⁴⁹,⁵⁰

In general, the interactions between polymer chains tend to broaden the absorption spectrum and thereby decrease the steepness of the UV-visible absorption spectrum.⁵¹–⁵³ Fig. 4 shows the steep UV-visible absorptions so it is likely that the main chains of the two polymers are well dissolved in dilute THF solution. The oscillator strength of the \( n \rightarrow \pi^* \) transition in the UV-visible absorption spectrum of PPQF is much smaller than that of the \( \pi \rightarrow \pi^* \) transition of the polymer backbone (\( \lambda_{\text{max}} = 370 \text{ nm}, \epsilon = 39800 \text{ L mol}^{-1} \text{ cm}^{-1} \)), indicating an efficient conjugation and intramolecular energy transfer from \( \pi \rightarrow \pi^* \) state to \( n \rightarrow \pi^* \) state as photoexcitation occurs. As a result, polymer PPQF exhibits very weak fluorescence at room temperature due to the intramolecular energy transfer from fluorescent \( \pi \rightarrow \pi^* \) state to non-fluorescent \( n \rightarrow \pi^* \) state of PQ in solution for the copolymer.

Many photochemical reactions of small molecular PQ have demonstrated that photochemical reactions proceed via the triplet excited state.⁵⁴,⁵⁵ Thus PPQF may have the advantages of efficient light harvesting through intramolecular energy transfer from both high-energy singlet and triplet \( \pi \rightarrow \pi^* \) excited states of the polymer backbone to the triplet \( n \rightarrow \pi^* \) excited state of PQ units. The photochemical reactions of small molecular PQ generally occur in homogeneous solution,⁶ while PQ incorporated in PPQF provides an opportunity of heterogeneous solid–liquid reaction, which is very significant for practical applications. Investigations of PPQF-based photochemical reactions are ongoing and the results will be presented elsewhere.

Electrochemistry
The electronic properties of the conjugated polymers are primarily governed by their chemical structure. Cyclic voltammetry (Table 2) provides an insight into the electro-activity and energy levels of the molecules. Figure 5 shows that both small molecular PQ and PPQF show quasi-reversible reduction waves corresponding to the PQ to PQ⁻ reduction couples.⁹ The detailed electrochemical data are summarized in Table 2. The electrochemical reduction enhances fluorescence of the PPQF film on an ITO (indium tin oxide) electrode, while the emission spectrum is recorded by performing the cyclic voltammetry at the same time. As the potential from 0 to −1.2 V versus \( \text{Fc/Fc}^+ \) is applied to the ITO conductive glass, a blue fluorescence arises at ca. −0.9 V versus \( \text{Fc/Fc}^+ \) and its intensity increases with increasing reduction potential (Fig. 5). The observed fluorescence is due to the electroreduction-induced conversion of the electronic state of the PQ segment from non-fluorescent \( n \rightarrow \pi^* \) PQ state to the fluorescent \( \pi \rightarrow \pi^* \) PQ⁻ state.

This observation is particularly important for the design of reduction-dependent receptors⁴ which sensor capability depends on the binding strength.
Our work demonstrates that palladium-catalyzed Suzuki coupling is an effective method for constructing a range of other polymers.

**CONCLUSIONS**

This study shows that palladium-catalyzed Suzuki coupling gives access to a well-defined, processable, electroactive conjugated copolymer PPQF. We have presented the synthesis, characterization and electro-optical properties of a novel PQ-containing conjugated copolymer using standard synthesis, physical and cyclic voltammetry methods. The presence of carbonyl functions in the copolymer increases the reduction activity, but reduces strongly the fluorescence quantum yield. The polymer has good solubility in common organic solvents such as CH₂Cl₂, CHCl₃ and THF. The polymer structure was verified using ¹H NMR, FTIR spectroscopy and elemental analysis. The properties of PPQF are compared with those of PDHF and PQ to provide better understanding. The polymer exhibited interesting electrochemical reduction activity and n → π⁺ electronic transitions when excited. The improved electrochemical behavior of PPQF compared to PDHF and molecular PQ shows its potential as a reduction-dependent sensor. The results provide a novel strategy for the design and construction of a range of other polymers.

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Study of a novel phenanthrenequinone-alt-dialkylfluorene conjugated copolymer