Polym. Bull. (2009) 63:37–46
DOI 10.1007/s00289-009-0066-7

ORIGINAL PAPER

Synthesis of porphyrin end-capped water-soluble poly(phenylene ethynylene) and study of its optical properties

Yongqing Xia · Jie Mao · Xin Lv · Yongsheng Chen

Received: 3 September 2008 / Revised: 11 March 2009 / Accepted: 18 March 2009 /

Abstract A novel Porphyrin End-Capped poly(phenylene ethynylene) (P-PPE) was synthesized by palladium-catalyzed cross-coupling reaction. Porphyrin was successfully introduced to the polymer backbone, which was confirmed by ^{1}H NMR, UV–Vis and Fluorescence spectroscopy. The degree of polymerization of P-PPE was characterized by both ^{1}H NMR and GPC analysis. UV–Vis absorption and fluorescence studies in organic solvent indicate that there is significant energy transfer between the PPE backbone and the terminal porphyrin end group, and the PPE backbone works as an antenna transferring photo energy to ZnTPP terminal. The aggregation state of P-PPE in water was also investigated by UV–Vis and fluorescence studies.

Keywords Poly(phenylene ethynylene) · Porphyrin · Synthesis · Optical property · Energy transfer · Aggregation state

Introduction

Conjugated polymers, particularly poly(phenylene ethynylene)s (PPEs) and poly(phenylene vinylene)s (PPVs), have been the focus of considerable research

Y. Xia (✉)
Center for Bioengineering and Biotechnology, China University of Petroleum (East China),
266555 Qingdao, People's Republic of China
e-mail: xiayq@upc.edu.cn

J. Mao (✉) · X. Lv · Y. Chen (✉)
Key Laboratory of Functional Polymer Materials, Ministry of Education,
Institute of Polymer Chemistry, Nankai University, 300071 Tianjin, People's Republic of China
e-mail: jmao2007@yahoo.cn

Y. Chen
e-mail: yschen99@nankai.edu.cn

and development during the past decades owing to their diverse functions and applications in fluorescence chemical sensors [1], light-emitting diodes [2], photoconductors and photovoltaic cells [3] etc. [4]. Environmentally friendly and water-soluble PPEs displaying optical and electronic properties have been proven useful, especially for fabrication of sensors for ions, peptides, proteins and nucleic acids [5, 6]. In such, different types of water-soluble PPEs [5, 7, 8] particularly nonionic water-soluble PPEs [5, 9–12] have been the interesting of many research groups recently.

Porphyrins are stable natural functional dyes with large visible extinction coefficient, predictable rigid structure, and prospective photochemical electron-transfer ability and they have been widely studied for various photo-harvesting and photoelectronic devices [13]. Covalent incorporation of photoactive molecules at the PPE end could lead to useful variations in the photophysical properties of this system [14, 15]. Recently, Krebs et al. [16] introduced the porphyrin unit into PPE backbone to form a porphyin linked PPE polymer (NPN) and studied its light-harvesting and energy transfer properties.

We report here the design and synthesis of porphyrin end-capped and non-ionic water-soluble PPE (Scheme 1) and its optical properties. The polar, non-ionic oligoethyleneglycol (OEG) side chains were introduced to enhance the usually poor solubility of the rigid backbone of PPEs. This OEG side chain could not only render the backbone soluble in a variety of media including water, but also provide a useful scaffold for further future functionalization. Moreover, this structure with excellent optical properties of both the PPE backbone and the end-cap offer an ideal model to study the energy transfer along the rigid chain and help us to design novel PPE polymers useful for optical or optoelectronic applications.

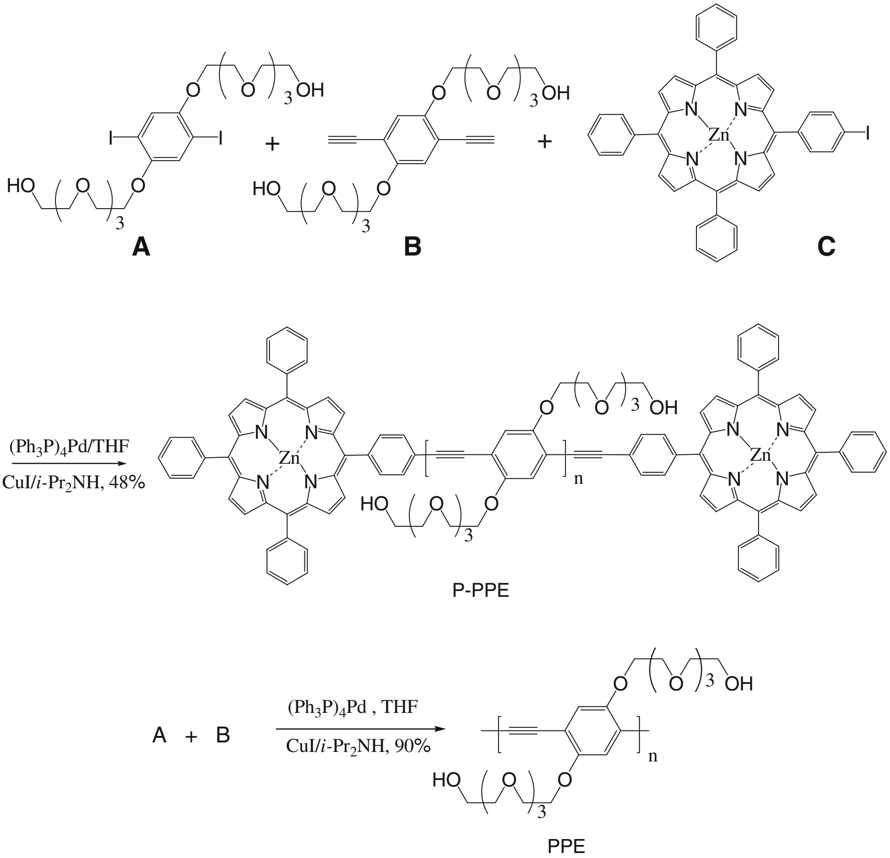
Experimental part

Materials

Unless otherwise indicated, all starting materials were obtained from Aldrich and were used without purification. Tetrahydrofuran (THF) was purified by distillation from sodium in the presence of benzophenone under argon. Other organic solvents were used without any further purification. [5-(4-iodophenyl)-10,15,20-triphenyl-prophinato]zinc[II] (Compound C) was synthesized according to the literature procedures[17]. All reactions were carried under argon. The synthesis of compound A, compound B and PPE (see Scheme 1) is according to our previous report [18].

Measurements

^{1}H NMR spectra were taken on a Bruker AVANCE 300 MHz spectrometer with TMS as the internal standard. UV-Vis spectra were recorded on a JASCO V-570 spectrophotometer at room temperature. Fluorescence measurement was carried out on a FluoroMax-P spectro-fluorophotometer with a xenon lamp as a light source. Mass spectra (MS) were obtained using a LCQ Advantage mass spectrometer at an



Scheme 1 Synthesis of the polymer P-PPE and PPE

ionizing voltage of 70 eV. Gel permeation chromatography (GPC) analysis was conducted with a Waters 510 HPLC system using polystyrenes as the standard, THF as eluent at a flow rate of 1.0 ml/min at 45 °C. Quantum yields were determined with quinine sulfate as the standard.

Synthesis of porphyrin end-capped PPE (P-PPE)

A 25 ml Schlenk flask equipped with a stir bar was charged with 1,4-Diethynyl-2,5-bis(11-hydroxy-3,6,9-trioxaundecyl)benzene (B, 25.5 mg, 0.05 mmol, 1.3 eq), 1,4-Diiodo-2,5-bis(11-hydroxy-3,6,9-trioxaundecyl)benzene (A, 25.5 mg, 0.036 mmol, 1 eq), [5-(4-iodophenyl)-10,15,20-triphenylprophinato]zinc[II] (C, 8 mg, 0.011 mmol, 0.3 eq), Tetrakis-(triphenyl-phosphine)-palladium(0) (3 mg 1.1 μmol, 0.07 eq) and copper(I) iodine (0.7 mg). The flask was degassed by three freeze-pump-thaw cycles after adding THF (10 ml) and diisopropylamine (0.8 ml) via a syringe needle. The reaction was stirred while maintaining the temperature at 55 °C for 48 h, then excess end capping reagent C was added to ensure a complete termination. Stirring was continued for further 12 h. The reaction was cooled to room temperature and then was poured into 50 ml hexane. The precipitate formed was collected by filtration and redissolved into chloroform and passed through a column of silica gel using the mixture of chloroform and methanol (1:1) as eluent. After concentrating in vacuum, P-PPE (29 mg, 48%) was obtained as a yellow-red solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.02 (s, 1.2H), 3.56–3.68 (br m, 20H), 3.79(br s, 4H), 3.93 (br s, 4H), 4.25 (br s, 4H), 7.08 (s, 2H), 7.77(m, 1.2H), 8.01(d, 1.2H), 8.22(m, 1.1H), 8.94 and 8.96(d, 1.0H). GPC (eluent: THF): $M_n = 10{,}485$, $M_w = 14{,}728$ and PDI = 1.4.

Results and discussion

Synthesis of P-PPE

We synthesized the polymers P-PPE according to Scheme 1 using Sonogashira coupling reaction by two subsequent steps. First, the polymerization was carried out with 30% excess of compound B to ensure the polymer chain was terminated by acetylene groups. Then, the initially formed polymer was end-capped in situ by reacting with an excess of the capping compound C. The polymer prepared by this procedure should be completely end-capped[15], because the average degree of polymerization (DP) estimated using the ^{1}H NMR end-group analysis [16] and the value obtained from the GPC analysis [18] are in excellent agreement with each other (see below). Comparing with PPE without porphyrin end groups (see Scheme 1), P-PPE exhibits good solubility in common organic solvents but less solubility in water, also indicating the hydrophobic porphyrin end groups were successfully incorporated into the polymer backbone.

GPC analysis shown that M_w and M_n of P-PPE were 14.7 and 10.5 kDa, respectively, indicating the degree of polymerization was about 18 (not include end groups) for P-PPE. The structure and the degree of polymerization of P-PPE were further confirmed by their ^{1}H NMR (Fig. 1). The signals of the protons of the porphyrin end group can be distinguished around $\delta = 7.8$–9.0 ppm that was not observed in the ^{1}H NMR spectrum of PPE [18]. On the basis of comparison of spectrum of the end-capped polymer P-PPE with that of zinc tetraphenylporphyrin (ZnTPP), as a model for the end-capped group in the polymer, it is believed that these peaks arise from the porphyrin end groups. Assuming the polymer was quantitatively end-capped with porphyrin group, we estimated the number-average degree of polymerization ($\overline{X}_n$) be 16 determined by the integration of the PPE phenyl group and Porphyrin group signals in ^{1}H NMR (Fig. 1) [19]. Note that the $\overline{X}_n$value determined by NMR integration is match well with that established by GPC for polymer P-PPE.

UV–Vis and fluorescence studies in chloroform solution

The absorption of P-PPE was investigated in chloroform solution and the spectra of PPE and ZnTPP were also investigated for comparison (Fig. 2a). PPE shows broad

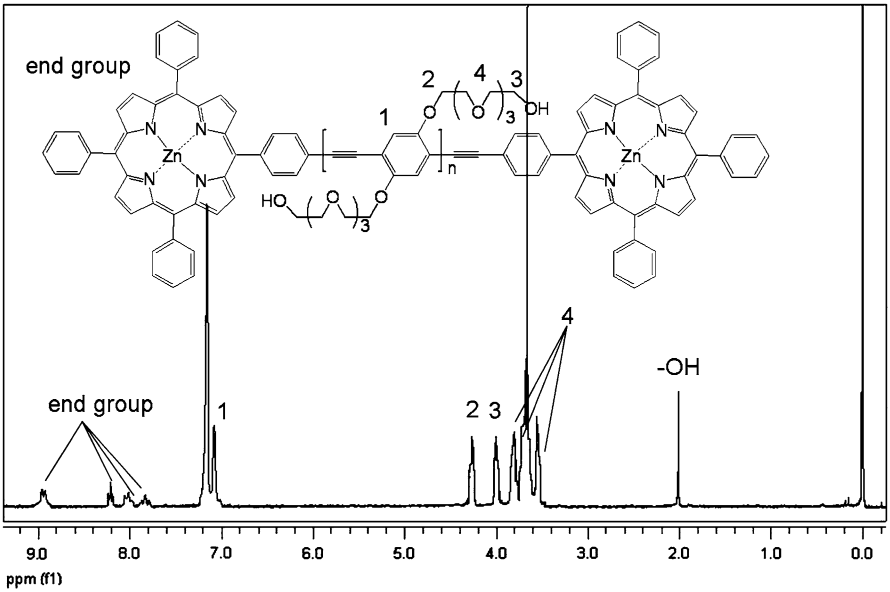


Fig. 1 ^{1}H NMR spectrum of P-PPE in $CDCl_3$ solvent

and intensive absorption in the range of 340–480 nm, and the absorption peak is observed at ~424 nm, corresponding to the effective conjugation along with the PPE backbone. The narrow and intensive absorption of porphyrin range from 390 to 430 nm, with sharp absorption peak at 419 nm. The absorption spectrum of P-PPE exhibited both absorption characteristics of PPE and porphyrin. Obviously, the broad absorption in the range of 340–480 nm and sharp absorption peak at 424 nm of P-PPE come from PPE backbone and ZnTPP, respectively, and the shoulder peak at ~400 nm also reveals the combination of PPE backbone and ZnTPP. Two weak but new absorption were observed at 554 and 594 nm for polymer P-PPE, corresponding to the porphyrin-based terminal group Q band. Furthermore, compared with the absorption spectrum of the terminal model compound ZnTPP, a considerable red shift (~8 nm) was observed for the Q-band for the porphyrin-based end unit. This indicates that some extended π-conjugation between the PPE backbone and the porphyrin terminal may be formed.

UV–Vis spectra can also be used to estimate the ratio of the PPE backbone and the terminal units in the polymer chain [16]. From the extinction coefficient for porphyrin model compound ZnTPP at 547 nm ($\in_{\mathrm{ZnTPP\ (547\ nm)}} = 30{,}400\ \mathrm{L\ M^{-1}\ cm^{-1}}$, $\in_{\mathrm{P\text{-}PPE\ (424\ nm)}} = 19{,}700\ \mathrm{L\ M^{-1}\ cm^{-1}}$ in $CHCl_3$) and the absorption ($\in_{\mathrm{P\text{-}PPE\ (554\ nm)}} = 800\ \mathrm{L\ M^{-1}\ cm^{-1}}$ in $CHCl_3$) of P-PPE at 554 nm, assuming it is due to the TPP cap group, we estimated that $\overline{X}_n$ is about 14, which is consistent with the estimation using ^{1}H NMR above.

Figure 2b shows that the fluorescence emission spectrum both excited at 420 nm for P-PPE and PPE. Both polymers were found to be highly fluorescent in solution and parallel the absorption spectra. The fluorescence properties of the polymers in

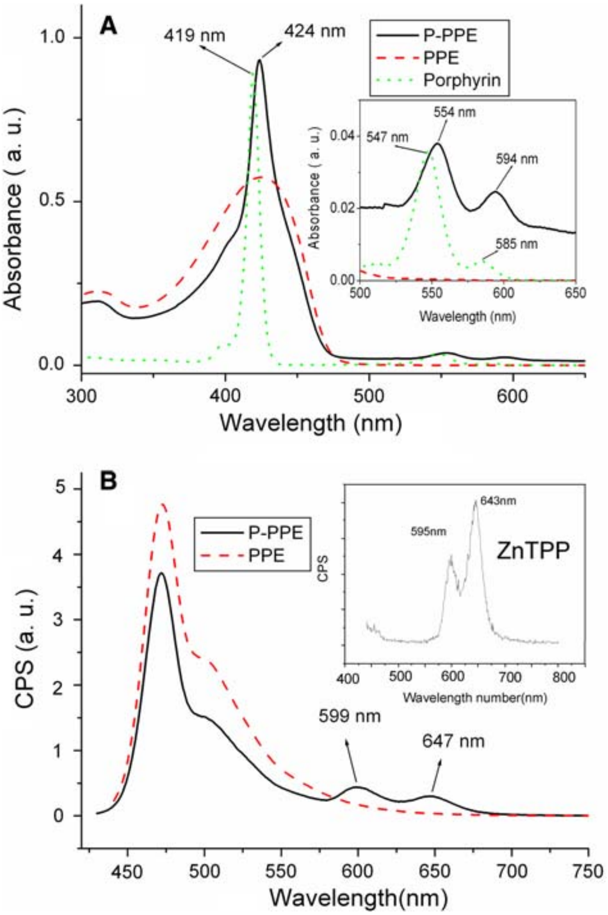


Fig. 2 UV–Vis (**a**) and fluorescence (**b**) spectra of P-PPE, PPE and ZnTPP in $CHCl_3$ solution

chloroform are very similar to those exhibited by organic-soluble PPEs in good solvents [4], suggesting that the polymer exists in a non-aggregated state in this medium. The intense fluorescence emission with similar pattern at 472 nm of PPE and P-PPE revealed that the polymers had similar backbone because no fluorescence emission of ZnTPP was found at this range (Fig. 2b inset). But, compared with PPE, the end-capped polymer P-PPE shows two new emission peaks at position 599 and 646 nm, near the emission peaks of corresponding model terminal compound ZnTPP (595 and 643 nm). The new emission of polymer P-PPE at 599 and 646 nm could come from either the intramolecular excition migration or direct emission of the porphyrin end group or both. One important issue we want to know is that whether there is an efficient energy/photo transfer between the PPE backbone and the terminal unit ZnTPP. Fortunately, we noticed that the new emission of polymer P-PPE at 599 and 646 nm of polymer P-PPE is relatively much stronger than that of the terminal model compound ZnTPP, considering the fractional content (~1/8 from NMR) of TPP unit in the polymer PPE. The energy transfer efficiency can be estimated by comparing the absorption and excitation spectra of the end-capped polymer P-PPE with that of ZnTPP [20]. For a very preliminary and rough estimation, considering the 16 of average degree of polymerization, we would expect the intensity of fluorescence at 595 nm from ZnTPP (Fig. 2 inset) should be roughly 7 times of that at 599 nm (Fig. 2b) from ZnTPP moiety in P-PPE, assuming the fluorescence from PPE backbone and ZnTPP units are independent each other and nonradicative decay is similar before and after incorporating these two moieties together as in P-PPE. In fact, with normalized corrected excitation spectra at 599 nm for P-PPE and 595 nm for ZnTPP at the same concentrations (0.001 mg/ml) for both solution, the fluorescence intensity of ZnTPP unit in P-PPE is much stronger ($\sim$20 times) than that of the model unit ZnTPP at 595 nm. While it is difficult now and premature to have an accurate result for the energy transfer efficiency and understanding of the transferring mechanism, these results do indicate that the PPE backbone is acting as an antenna, transferring photo energy to ZnTPP terminal and enhancing over 20-fold the emission from it. This also agrees with the decreasing of fluorescence intensity of P-PPE at 472 nm compared with that of PPE and their quantum yields ($\varphi_{\mathrm{PPE}} = 0.35$, $\varphi_{\mathrm{P\text{-}PPE}} = 0.27$ in $CHCl_3$).

UV–Vis and fluorescence studies in water solution

We intend to use these polymers in water solutions. So their absorption and fluorescence were studied in water solutions too (Fig. 3). Both UV–Vis spectra of polymer PPE and P-PPE shows (Fig. 3a) a significant red-shift and decrease for their major band absorption ($\epsilon_{\mathrm{PPE}} = 13{,}900$ L M^{-1} cm^{-1}, $\epsilon_{\mathrm{P\text{-}PPE}} = 12{,}700$ L M^{-1} cm^{-1} in H_2O; $\epsilon_{\mathrm{PPE}} = 20{,}300$ L M^{-1} cm^{-1}, $\epsilon_{\mathrm{P\text{-}PPE}} = 19{,}900$ L M^{-1} cm^{-1} in $CHCl_3$) compared with that in chloroform. For P-PPE, interestingly the major absorbance exhibited two peaks at the position of 434 and 472 nm. We argue this may be caused by the existence of two states of P-PPE in water solution: one is the less aggregated or monomeric state and the other one is the aggregated state. The red-shift band (472 nm) is due to planarization of the conjugated main chain by formation of polymer aggregates [21, 22]. Two weak absorptions at 554 and 594 nm observed in spectrum in $CHCl_3$ solution were still exhibited as two weak peaks at 563 and 603 nm in water solution, indicting the change of electronic state of porphyrin, however it was minor affected by the existing state of polymer backbone. The "solvatochromic effect" indicates we are able to finely tune the photo properties of this polymer by simply changing the solvents [21–24].

Similar red shift was observed for their fluorescence spectra (Fig. 3b), compared with that in chloroform solution. For examples, the major peak for PPE and P-PPE had $\sim$44 nm red shift. Furthermore, the fluorescence spectra become much broad and the major emission peaks extend to $\sim$700 nm. Broad, structureless emission is typically observed from small-molecule excimers and from conjugated polymer in the solid state [8, 25] and it has been well known that the interchain π–π stacking will cause the rod-like polymers to aggregate in water and thus exhibit a broad and red-shift fluorescence spectrum. Quantum yields of PPE and P-PPE were 0.046 and 0.035, respectively, in water, significantly lower than that in chloroform. This

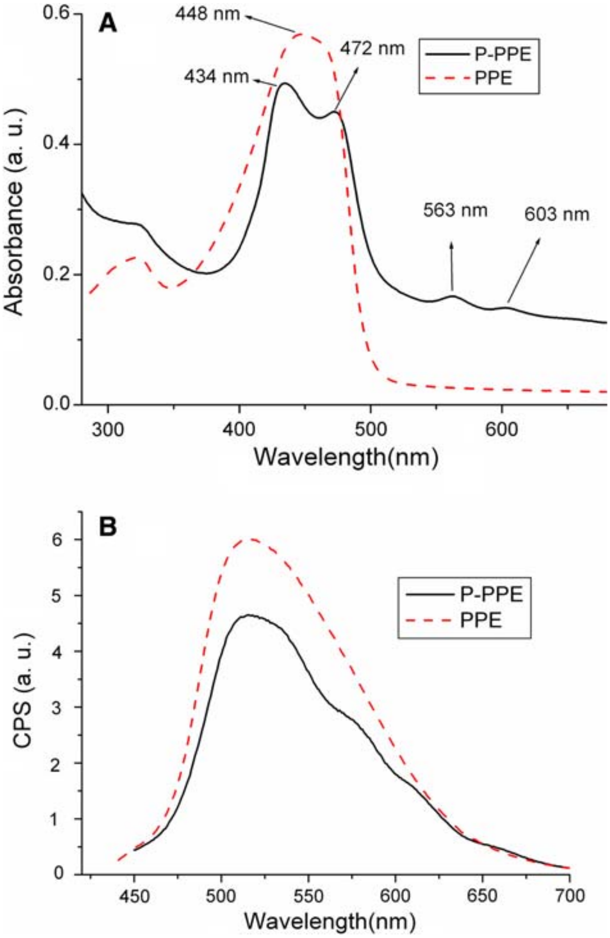


Fig. 3 UV–Vis (**a**) and fluorescence (**b**) spectra of P-PPE, PPE in water

indicates that in water, the stronger inter-chain π–π interactions from the aggregation provide more non-emission decay channels for the excited state [26]. This is also supported by the larger stokes shifts in water solutions: 70 and 81 nm in water versus 44 and 48 nm in chloroform for PPE and P-PPE respectively. We thus believe, though both polymers have relatively good solubility in water, still some aggregation happens in the water solutions to result in the broad and red-shift fluorescence spectra and this aggregation is stronger for P-PPE due to the existing of end ZnTPP group.

Conclusion

In the present investigation, nonionic water-soluble and porphyrin end-capped polymer P-PPE was synthesized by palladium-catalyzed cross-coupling reaction and photophysical properties of P-PPE and PPE have been studied. Both PPE and P-PPE exhibit good solubility in organic solvents, more importantly in water. UV–Vis absorption and fluorescence studies indicate that there is significant energy transfer between the PPE backbone and the terminal porphyrin end group and the PPE backbone works as an antenna transferring photo energy to ZnTPP terminal. This makes them a good choice for water-processible polymers for various photonic and optoelectronic applications.

Acknowledgments The authors gratefully acknowledge the financial support from the NSF (#20644004, 60676051 and 20804057) of China.

References

1. McQuade DT, Pullen AE, Swager TM (2000) Conjugated polymer-based chemical sensors. Chem Rev 100:2537–2574
2. Veinot JGC, Marks TJ (2005) Toward the ideal organic light-emitting diode. The versatility and utility of interfacial tailoring by cross-linked siloxane interlayers. Acc Chem Res 38:632–643
3. Mwaura JK, Pint MR, Witker D, Ananthakrishnan N, Schanze KS, Reynolds JR (2005) Photovoltaic cells based on sequentially adsorbed multilayers of conjugated poly(p-phenylene ethynylene)s and a water-soluble fullerene derivative. Langmuir 21:10119–10126
4. Bunz UHF (2000) Poly(aryleneethynylene)s: syntheses, properties, structures, and applications. Chem Rev 100:1605–1644
5. Xue CH, Chen Z, Luo FT, Palaniappan K, Chesney DJ, Liu J, Chen J, Liu HY (2005) Synthesis of water-soluble electroactive ferrocene-grafted poly(p-phenylene-ethynylene) via phase transfer and its biosensing application. Biomacromolecules 6:1810–1815
6. Wosnick JH, Mello CM, Swager TM (2005) Synthesis and application of poly(phenylene ethynylene)s for bioconjugation: a conjugated polymer-based fluorogenic probe for proteases. J Am Chem Soc 127:3400–3405
7. Fan QL, Zhou Y, Lu XM, Hou X, Huang W (2005) Water-soluble cationic poly(p-phenyleneethynylene)s (PPEs): effects of acidity and ionic strength on optical behavior. Macromolecules 38:2927–2936
8. Pinto MR, Kristal BM, Schanze KS (2003) A water-soluble poly(phenylene ethynylene) with pendant phosphonate groups. Synthesis, photophysics, and layer-by-layer self-assembled films. Langmuir 19:6523–6533
9. Khan A, Muller S, Hecht S (2005) Practical synthesis of an amphiphilic, non-ionic poly(para-phenyleneethynylene) derivative with a remarkable quantum yield in water. Chem Commun 584–586
10. Kim IB, Erdogan B, Wilson JN, Bunz UHF (2004) Sugar–poly(para-phenylene ethynylene) conjugates as sensory materials: efficient quenching by Hg^{2+} and Pb^{2+} ions. Chem Eur J 10:6247–6254
11. Kuroda K, Swager TM (2003) Synthesis of a nonionic water soluble semiconductive polymer. Chem Commun 26–27
12. Lavigne JJ, Broughton DL, Wilson JN, Erdogan B, Bunz UHF (2003) "Surfactochromic" conjugated polymers: surfactant effects on sugar-substituted PPEs. Macromolecules 36:7409–7412
13. Holten D, Bocian DF, Lindsey JS (2002) Probing electronic communication in covalently linked multiporphyrin arrays. A guide to the rational design of molecular photonic devices. Acc Chem Res 35:57–69
14. Funston AM, Silverman EE, Miller JR, Schanze KS (2004) Charge transfer through terthiophene end-capped poly(arylene ethynylene)s. J Phys Chem B 108:1544–1555
15. Nesterov EE, Zhu ZG, Swager TM (2005) Conjugation enhancement of intramolecular exciton migration in poly(p-phenylene ethynylene)s. J Am Chem Soc 127:10083–10088
16. Nielsen KT, Spanggaard H, Krebs FC (2005) Synthesis, light harvesting, and energy transfer properties of a zinc porphyrin linked poly(phenyleneethynylene). Macromolecules 38:1180–1189
17. Syrbu SA, Semeikin AS, Berezin BD (1990) Synthesis of tetraphenylporphines with active groups in the phenyl rings 6. Synthesis of monosubstituted tetraphenylporphines by diazotization. Chem Heterocycl Comp 26:1255–1257

18. Mao J, Liu Q, Lv X, Liu ZF, Huang Y, Ma YF, Chen YS, Yin SG (2007) A water-soluble hybrid material of single-walled carbon nanotubes with an amphiphilic poly(phenyleneethynylene): preparation, characterization, and photovoltaic properties. J Nanosci Nanotechnol 7:2709–2718
19. Palmans ARA, Smith P, Weder C (1999) Polarizing energy transfer in photoluminescent conjugated polymers with covalently attached sensitizers. Macromolecules 32:4677–4685
20. Devadoss C, Bharathi P, Moore JS (1996) Energy transfer in dendritic macromolecules: molecular size effects and the role of an energy gradient. J Am Chem Soc 118:9635–9644
21. Halkyard CE, Rampey ME, Kloppenburg L, Studer-Martinez SL, Bunz UHF (1998) Evidence of aggregate formation for 2,5-dialkylpoly(p-phenyleneethynylenes) in solution and thin films. Macromolecules 31:8655–8659
22. Wang YQ, Zappas AJ, Wilson JN, Kim IB, Solntsev KM, Tolbert LM, Bunz UHF (2008) Optical spectroscopy of grafted poly(p-phenyleneethynylene)s in water and water–DMF mixtures. Macromolecules 41:1112–1117
23. Belletete M, Bouchard J, Leclerc M, Durocher G (2005) Photophysics and solvent-induced aggregation of 2,7-carbazole-based conjugated polymers. Macromolecules 38:880–887
24. Zheng M, Ding LM, Gurel EE, Lahti PM, Karasz FE (2001) Oxadiazole containing conjugated–nonconjugated blue and blue-green light emitting copolymers. Macromolecules 34:4124–4129
25. Kim Y, Bouffard J, Kooi SE, Swager TM (2005) Highly emissive conjugated polymer excimers. J Am Chem Soc 127:13726–13731
26. Lu SL, Yang MJ, Bai FL (2004) Synthesis, electrochemical, and optical properties of a novel PPV/PPE block-copolymer. Macromol Rapid Commun 25:968–971