



Tuning the backbones and side chains of cationic meta-linked poly(phenylene ethynylene)s: Different conformational modes, tunable light emission, and helical wrapping of multi-walled carbon nanotubes



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ABSTRACT

We have an ongoing interest in the design and control of helical conformation of water-soluble meta-linked poly(phenylene ethynylene)s (PPEs) and the further development of novel functional materials. Four cationic meta-linked PPEs (P1'–P4') were synthesized to study the influence of differences in the backbone and side chain structure on their conformations. For P1' and P4' without side chains on the *para*-phenylene units, fluorescence spectroscopic investigations indicated obvious intramolecular helical folding, whereas for P2' and P3' with nonpolar and polar side chains on the *para*-phenylene units respectively, a significantly different conformational mode, namely, cofacial intermolecular aggregation was suggested. The side chains on the *para*-phenylene units of P2' and P3' may be located in the interior cavity of helix and induce steric effect on the formation of helix. However, the introduction of 2,1,3-benzothiadiazole (BT), a low energy gap unit, into the backbone of P4' showed little influence on the formation of helix despite its larger and more rigid structure than the phenylene unit. Thus, the light emission of these polymers can be tuned in the range from blue, green to yellow with the changes of conformational modes. Moreover, the functionalization of multi-walled carbon nanotubes (MWCNTs) by P4' in methanol and water, and by using its neutral precursory polymer P4 in tetrahydrofuran was explored through transmission electron microscopy and fluorescence spectroscopy. P4' was directly observed to individualize MWCNT by forming a monolayer helical wrapping on the nanotube surface, which may be attributed to the backbone flexibility of meta-linked PPE and the strong π – π interactions between the PPE backbone and the CNT surface. Moreover, P4' served as a better dispersing agent for MWCNT than P4, suggesting that the cationic side groups may act as solubilizing groups which also separated the individual nanotubes because of charge repulsion.

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1. Introduction

The development of synthetic helical polymers and oligomers (foldamers) may lead to a better understanding of the mechanisms for helix formation and complicated functions in biopolymers, and thus help create novel functional materials [1–7]. π -Conjugated helical polymers have been under hot pursuits because of their potential applications based on the formation of helical conformation, such as unique optical and electronic materials for

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molecular recognition (separation, sensory functions), chiral materials, and building blocks for self-assembled nanomaterials and devices [8–13]. The design and control of helical conformation of π -conjugated polymers is still an intriguing and challenging subject.

Water-soluble poly(phenylene ethynylene)s (PPEs) are a kind of π -conjugated polymer whose unique optical properties have led to applications in chem/bio sensors [14–17]. The self-assembly of water-soluble PPEs has recently also been intensively investigated owing to their amphiphilic structure, relatively free internal rotation of alkyne-aryl single bond and favorable π - π interactions between planar phenylene units [18–27]. Moreover, water-soluble meta-linked PPEs have been demonstrated to provide desirable flexibility for helical folding due to the presence of *meta*-phenylene unit in the conjugated backbone [19,24–27]. Schanze and co-workers have reported solvent-induced helix formation of anionic water-soluble, meta-linked PPEs, which were able to template the formation of supramolecular helical aggregates of dye molecules [24,25]. Our group has synthesized a cationic meta-linked polymer *m*-PPE- NET_2Me^+ which exhibited unique solvent- and pH-induced helix formation, and studied the effects of helix formation on amplified fluorescence quenching and fluorescence resonance energy transfer (FRET) in chem/bio sensors [26]. On the basis of previous studies, we have an ongoing interest in the design and control of helical conformation of water-soluble meta-linked PPEs and the further development of novel functional materials.

Stabilization of helical conformation is believed to be influenced by the factors including solvophobic interactions [28,29], π - π stacking of aromatic units [23,24] and steric effects [30,31]. It is possible to manipulate supramolecular architectures by modifying the composition of π -conjugated backbones or subtle structure of aromatic rings because π - π stacking tendencies are strongly influenced by the properties of interacting aromatic rings. Hence, in this research, we tuned the backbones and side chains of the cationic meta-linked PPEs and synthesized a series of polymers P1'-P4'. In comparison with previously reported *m*-PPE- NET_2Me^+ , P1'-P4' exhibited different linking groups between the cationic side groups and the backbones. Moreover, nonpolar and polar side chains were introduced to the *para*-phenylene units of P2' and P3', respectively, and 2,1,3-benzothiadiazole (BT) units with low energy gap were introduced into the conjugated backbone of P4'. We observed an obvious difference in the optical properties between cationic meta-linked PPEs with and without side chains on the *para*-phenylene units. Fluorescence spectroscopic investigations indicated the intramolecular helical folding of P1' and P4' in water, and the significantly different conformational mode, namely, cofacial intermolecular aggregation for P2' and P3'. The side chains on the *para*-phenylene units of P2' and P3' may be located in the interior cavity of helix and induce steric effect; however, the introduction of BT showed little influence on the formation of helix despite its larger and more rigid structure than the phenylene unit. Thus, the light emission of these polymers can be tuned in the range from blue, green to yellow.

Based on the understanding of folding processes of these polymers, we were prompted by the rich conformational flexibility of meta-linked PPEs to study their composites with carbon nanotubes (CNT). Flexible polymers provide structures capable of wrapping CNT surface and enhance the solubility of CNT in solutions through noncovalent functionalization while still preserving nearly all of CNT's intrinsic properties [32–34]. Moreover, some π -conjugated polymers can be used to sort CNTs with different diameters to achieve optimum performance of CNT in various applications [19,35,36]. It has been established that π -conjugated polymer/CNT composites often exhibit synergistic optoelectronic effects such as dramatically enhanced conductivities and charge mobilities

[37–40]. However, few studies have been reported in the functionalization of CNT by using meta-linked PPE. Pang et al. reported an anionic meta-linked PPE whose helical conformation preferred to selectively host the CNTs of comparable sizes [19]. Herein, the functionalization of MWCNT by using the cationic meta-linked P4' in methanol and water, and by using its neutral precursory polymer P4 in tetrahydrofuran (THF) was explored through transmission electron microscopy (TEM) and fluorescence spectroscopy. P4' was directly observed to individualize MWCNT by wrapping the nanotube surface and forming a well-defined helix; moreover, it served as a better dispersing agent for MWCNT than its neutral precursory polymer.

2. Experimental section

2.1. Materials

All chemical reagents used in the synthesis of the polymers were purchased from either Acros or Aldrich Chemical Co. and used without further purification. Multi-walled carbon nanotubes (MWCNTs, purity >95%, ID: 5–12 nm, OD: 30–50 nm, and Length: 1–2 μm) were procured from TimesNano, Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. All aqueous solutions were prepared with MilliQ water (18.2 MQ cm) from a Millipore system. 3,5-Diiodobenzoic acid (1) [25], 1,4-diethynylbenzene (Monomer 2) [41], 1,4-dimethoxy-2,5-diiodobenzene (2) [42], 1,4-diiodo-2,5-hydroquinone (4) [42] and 4,7-dibromobenzothiadiazole (7) [43] were synthesized according to the literature procedures.

2.2. General methods

NMR spectra were collected on a Bruker Ultra shield Plus 400 spectrometer with tetramethylsilane as the internal standard. UV-Vis absorption spectra were taken on a Shimadzu 3600 PC spectrophotometer. Photoluminescence measurement was carried out on a Shimadzu RF-5301 PC spectrofluorophotometer with a xenon lamp as a light source. Photoluminescence quantum yields were obtained on an Edinburgh FLSP920 Instrument. Photographs were recorded on a digital camera (Canon 60D, Japan). Elemental microanalyses were carried out on a Vario EL III CHNOS Elemental Analyzer. Mass spectra were taken on a Shimadzu GCMS-QP2010 plus equipped with DB-5 ms column. The gel permeation chromatography (GPC) measurement was performed by Shimadzu Shim-pack GPC-800 system against polystyrene standards with tetrahydrofuran (THF) as the eluent. The differential scanning calorimetry (DSC) analyses were performed on a Shimadzu DSC-60A instrument under a heating rate of 10 $^{\circ}\text{C}/\text{min}$ and a nitrogen flow rate of 10 cm^3/min . Transmission electron microscopy (TEM) images were obtained with a JEOL 2010 transmission electron microscope at an accelerating voltage of 100 kV.

The optical properties of polymers were studied in dilute solutions ($c = 2 \times 10^{-5}$ mol/L, based on polymer repeat unit). All fluorescence spectra were recorded in a 3 mL quartz cuvette with an optical path length of 1.0 cm.

Preparation of P4'/MWCNT composite was performed by using the standard sonication-centrifugation technique [21,44]. A methanol or aqueous solution of the P4' (5 mL, 1×10^{-4} mol/L) was mixed with MWNTs (2 mg) in a vial. The mixture was sonicated for 10 min at 66% amplitude using a probe sonicator (Ultrasonic processor 130 W model, Sonics, Newtown, CT). A water bath (250 mL) was placed outside the vial to keep the temperature at ~ 25 $^{\circ}\text{C}$. During sonication processes, the mixture was removed from the sonication tip at 2 min intervals and vortexed for 20 min. Upon completion, the mixture was transferred to two centrifuge tubes in

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