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Cationic phenyl-substituted poly(*p*-phenylenevinylene) related copolymers with efficient photoluminescence and synthetically tunable emissive colors

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Abstract

A series of amino-functionalized phenyl-substituted poly(*p*-phenylenevinylene) (PPV) related copolymers were synthesized by Wittig reaction. Their corresponding cationic conjugated polymers were successfully obtained via a post-polymerization approach. On the basis of FT-IR and ^{1}H NMR spectra, it was found that phenyl-substituted PPV related copolymers containing alkoxylated benzene (neutral polymer **P1** and quaternized polymer **P1′**), phenylated benzene (neutral polymer **P2** and quaternized polymer **P2′**) and fluorene (neutral polymer **P3** and quaternized polymer **P3′**) moieties are of 55, 80, and 45% *cis*-vinylic linkage respectively while the polymer containing thiophene moiety (neutral polymer **P4** and quaternized polymer **P4′**) is primarily of *trans*-vinylic linkage. Their photoluminescence (PL) were conveniently tuned from blue color to yellow color by introducing units with different optoelectronic properties into the PPV backbones. The polymer with fluorene unit and bulky phenylene-substituted benzene unit in the backbone exhibited the highest PL efficiency among these neutral and quaternized PPVs. **P4′** containing little *cis*-vinylic linkage showed complete quenching while **P1′**–**P3′** containing much more *cis*-vinylic linkage showed incomplete quenching, indicating that the quenching behavior of these cationic PPVs may be highly influenced by the content of *cis*-vinylic linkage in the PPV backbones.

Keywords: Cationic conjugated polymer; Poly(*p*-phenylenevinylene); Fluorescence quenching

1. Introduction

Poly(*p*-phenylenevinylene) (PPV) and its derivatives have attracted a great deal of attention in recent years because of their interesting electroluminescent properties and their potential application as the active emitting layer in light-emitting diodes (LEDs) [1]. Recently, considerable research has focused on anionic PPVs (mainly sulfonated PPVs), which are the good candidates as chemo or biosensors that exhibit rapid and collective response to relatively small perturbations in local environments [2–6]. Such amplified fluorescence quenching is achieved by electron transfer or energy transfer due to the facile energy migration along the conjugated backbone and the relatively strong electrostatic binding of the oppositely charged quenchers with ionic conjugated polymers [7]. Although anionic PPVs exhibit remarkable optoelectronic properties and have been reported on detecting proteins for biological target by electron transfer [2], these polymers suffer from their intrinsic shortcomings such as relatively low photoluminescence (PL) quantum efficiency and their anionic charges that cannot be used to detect anionic biomolecules by electrostatic attraction.

Most recently, cationic fluorescent conjugated polymers were successfully developed to analyze anionic quencher [8] and anionic DNA [9–13] by energy transfer. To obtain highly efficient energy transfer and therefore improve the sensitivity, new types of cationic conjugated polymers with suitable emission wavelength and high PL efficiency are

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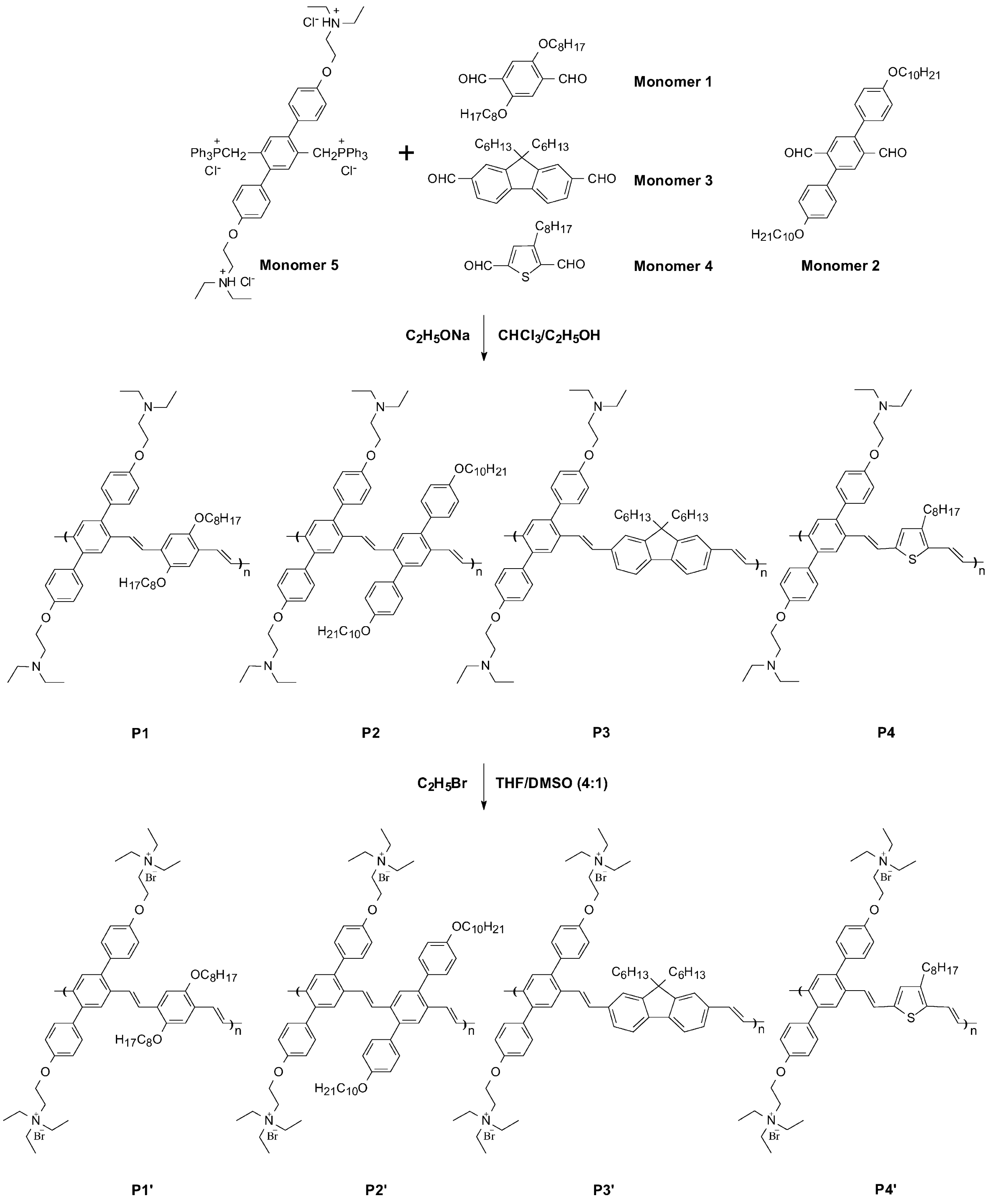
required. PPV is very appropriate for the color tunability over the full visible range by the control of its HOMO–LUMO band gap and for enhancement of the PL quantum efficiency under introduction of bulky group into the side chain or incorporation of unit with high PL efficiency into the conjugated main chain [1]. Therefore, it is crucial to develop cationic PPVs with higher PL quantum efficiency and different emission wavelength to evaluate a variety of polymer compositions for obtaining optimized sensory materials.

In this paper, we report the successful syntheses of cationic phenyl-substituted PPV related copolymers. Their emissive color was tuned by introducing arene units with different electronic properties. Furthermore, we attempted



Scheme 1. The synthetic routes for the neutral and quaternized polymers.