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Synthesis of a novel cationic water-soluble efficient blue photoluminescent conjugated polymer

Bin Liu,[a] Wang-Lin Yu,[b] Yee-Hing Lai*[a] and Wei Huang*[b]

[a] *Department of Chemistry, National University of Singapore, Singapore 119260, Republic of Singapore*
[b] *Institute of Materials Research and Engineering (IMRE), National University of Singapore, 3 Research Link, Singapore 117602, Republic of Singapore. E-mail: wei-huang@imre.org.sg*

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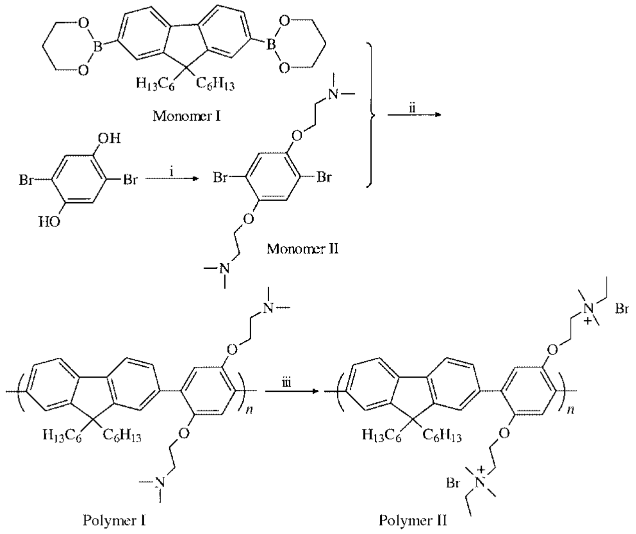
A novel cationic conjugated polymer, poly[(9,9-dihexyl-2,7-fluorene)-*alt-co*-(2,5-bis{3-[(*N*,*N*-dimethyl)-*N*-ethylammonium]-1-oxapropyl}-1,4-phenylene)] dibromide, which is water-soluble and emits bright blue fluorescence both in solutions and as films, is synthesized through Suzuki coupling reaction and a post-polymerization treatment.

Water-solubility of conjugated polymers may offer many new application opportunities. Potential applications of water-soluble conjugated polymers include the construction of active layers in organic light-emitting diodes through a layer-by-layer self-assembly approach,[1] as buffer layer and emissive layer materials in inkjet printing fabricated organic LEDs,[2] and as highly sensitive fluorescent sensory materials in living bodies.[3] Such applications generally favor high molecular weights and high photoluminescence (PL) efficiencies and require different ionic types. Water-solubility of semiconducting conjugated polymers was first demonstrated in 3-substituted polythiophenes[4,5] and was then extended to poly(*para*-phenylene vinylene) (PPV)-based[6] and poly(*para*-phenylene) (PPP)-based polymers.[7,8] The water-solubility in such polymers was achieved by functionalizing the substituted side chains with terminal carboxylate or sulfonate groups. These polymers are, therefore, anionic polyelectrolytes. Until the most recent report on the synthesis of ammonium-functionalized PPPs from Reynolds' group,[9] there are no cationic water-soluble conjugated polymers available. Fluorene-based conjugated polymers have received considerable attention in the past few years for the high efficiencies both in PL and in electroluminescence (EL).[10] Moreover, we recently demonstrated that conjugated polymers based on alternating fluorene and phenylene backbones are promising efficient and stable blue luminescent materials.[11] This work presents the successful effort in developing a cationic water-soluble conjugated polymer based on the alternating fluorene and phenylene backbone, which represents the first example of fluorene-based water-soluble conjugated polymer and exhibits efficient blue light emission.

The chemical structure of the new water-soluble conjugated polymer, poly[(9,9-dihexyl-2,7-fluorene)-*alt-co*-(2,5-bis{3-[(*N*,*N*-dimethyl)-*N*-ethylammonium]-1-oxapropyl}-1,4-phenylene)] dibromide (PFP-NMe$_2$EtBr) and the synthetic route are depicted in Scheme 1. Monomer I, 9,9-dihexylfluorene-2,7-bis(trimethylene boronate), was synthesized from 2,7-dibromofluorene as the starting material.[11] Monomer II, 2,5-bis[3-(*N*,*N*-dimethylamino)-1-oxapropyl)-1,4-dibromobenzene], was prepared from 2,5-dibromohydroquinone by reaction with 2-chloroethyldimethylamine in refluxing acetone in the presence of an excess of anhydrous potassium carbonate.[9] The polymerization was carried out in a mixture of toluene and aqueous potassium carbonate solution (2 M) containing 1 mol% Pd(PPh$_3$)$_4$ under vigorous stirring at 85–90 °C for three days. The neutral polymer, polymer I, was obtained as a fibrous white solid with a yield of *ca*. 70% after purification and drying. Conversion of the neutral polymer to the final water-soluble polymer was achieved by treatment with bromoethane in dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) (1 : 4).



Scheme 1 Chemical structures and synthetic route towards the polymers. *Reagents and conditions*: i, 2-chlorotrimethylamine hydrochloride, anhydrous potassium carbonate, acetone, reflux, 3 days; ii, toluene/aqueous potassium carbonate solution (2 M), Pd(PPh$_3$)$_4$, 85–90 °C, 3 days; iii, bromoethane, DMSO–THF (1 : 4), 50 °C, 3 days.

The structures of both the neutral and the final water-soluble polymers were confirmed by NMR and elemental analysis.†

The characterization of molecular weight is often a problem for water-soluble conjugated polymers. The post-polymerization approach for the realization of water-solubility allows us to characterize the molecular weight at the stage of the neutral polymer. The neutral polymer, polymer I, can be readily dissolved in CHCl$_3$, THF, toluene and aqueous acid, but is insoluble in DMSO, methanol and water. Gel-permeation chromatography (GPC) measurement using THF as eluent and polystyrenes as the standards indicated the weight average molecular weight to be 47 000, with a polydispersity of 1.61. Another advantage of the post-polymerization approach is that the quaternization degree can be controlled and thus the water-solubility of the resultant polymer is tunable. The tunable solubility is useful for the application of such materials as buffer layers in inkjet printing fabrication of LEDs.[2] The degree of quaternization could be determined by ^{1}H NMR spectra. As shown in Fig. 1, the neutral polymer exhibits three peaks in the region δ 7.8–7.6 arising from the aromatic protons in fluorene and one peak at δ 7.15 due to the protons in the phenylene ring. The well resolved peaks at δ 4.09, 2.67 and 2.30 correspond to methylene groups adjacent to the oxygen (–OCH$_2$–) and nitrogen (–CH$_2$N–) atoms and the methylamino groups (–NCH$_3$), respectively. After the treatment with bromoethane, the peaks in the aromatic region remain almost unchanged, whereas all the signals corresponding to –OCH$_2$–, –CH$_2$N–, and –NCH$_3$ split into two peaks, which arise from the quaternarized (lower field) and un-quaternized components, respectively. The

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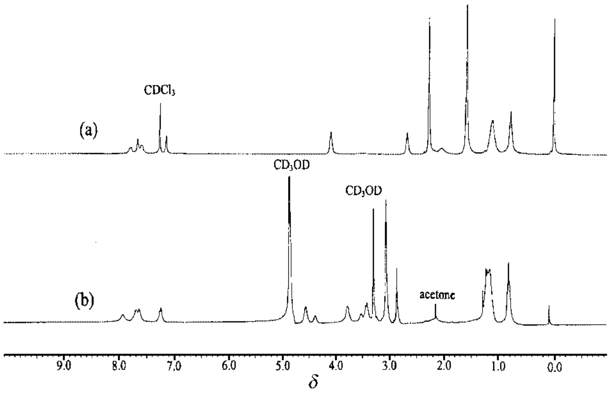

Fig. 1 ^{1}H NMR spectra of polymers I (a) and II (b).

relative integrals of each pair of the split peaks can thus be used to estimate the degree of quaternization. The highest degree of quaternization obtained in our experiments is *ca*. 80%. With this degree of quaternization, the resulting polymer shows solubility characteristics opposite to that of polymer I, being completely soluble in DMSO, methanol, and water but insoluble in CHCl$_3$ and THF.

Polymer II also possesses good thermal stability. The onset degradation temperature of this polymer is 300 °C in nitrogen, whereas it starts to decompose above 230 °C in air, with a small amount of water loss at lower temperatures. In air, no residue remained after heating to 800 °C.

The UV–VIS absorption spectra of polymer I in chloroform solution and as a film (on quartz plate, spin-cast from chloroform solution) are almost identical with the same maximum absorption at 366 nm. The PL spectrum of the polymer solution peaks at 414 nm, whereas the polymer film exhibits an emission maximum at 424 nm with a vibronic shoulder around 444 nm. The emission spectral feature of the polymer in the film state is very similar to that of the polymer having the same backbone structure and substitution on fluorene unit but without the terminal amino group in the phenylene side chains.[11] This implies that the terminal amino groups are unlikely to affect the conformation of the backbone in the film state. For the quaternized sample with the highest degree of quaternization (*ca*. 80%), the electronic spectra are remarkably dependent on the solvent, showing a bathochromic shift with a decrease in solvent polarity. As displayed in Fig. 2, the polymer shows absorption maxima at 343, 354 and 367 nm in water, methanol and DMSO, respectively. The corresponding PL maxima appear at 409, 409 and 419 nm, respectively. Uniform and transparent films of the polymer on quartz plates were prepared by spin-casting its aqueous solution. The UV–VIS absorption and PL spectra of the polymer film are also shown in Fig. 2. The absorption and emission peaks appear at 359 and 416 nm, respectively.

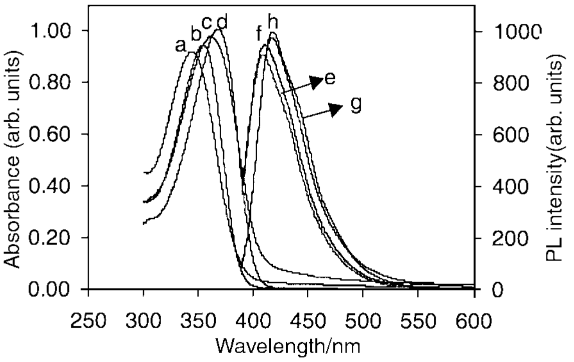

Fig. 2 UV–VIS absorption and photoluminescence spectra of polymer II in solutions and as films. (a) UV in aqueous solution, (b) UV in MeOH, (c) UV in film, (d) UV in DMSO, (e) PL in MeOH, (f) PL in aqueous solution, (g) PL as film and (h) PL in DMSO.

From the application point of view, one of the most attractive properties of the polymers is the relatively high PL quantum yield (Φ_{pl}). Both the neutral polymer and the quaternized polymers display strong blue fluorescence either in solutions or as films upon exposure to UV light. The Φ_{fl} of the neutral polymer (polymer I) is as high as 97% as measured from its dilute solution in chloroform.‡ For polymer II (with a degree of quaternization of 80%), the Φ_{pl} was measured to be 86% from its dilute solution in methanol. When the measurement was conducted in aqueous solution, the corresponding value of Φ_{pl} is 25%. The decrease of PL efficiency may be attributed to the aggregation of the polymer in aqueous solution. This was supported by a further reduced PL efficiency measured in the solid state (films on quartz plate cast from methanol solution), which is 4% compared with 9,10-diphenylanthracene as standard (dispersed in PMMA films with a concentration lower than 1×10^{-3} M, assuming a PL efficiency of 83%).[12]

In summary, we have synthesized a new cationic water-soluble conjugated polymer based on the alternating fluorene and phenylene backbone structure through a facile post-polymerization approach, which permits a full structural characterization of the polymer and control of the degree of cation formation. The polymer emits intense blue fluorescence both in solutions and in film states. The good water-solubility and high fluorescence quantum yield make it attractive for applications in fabricating organic LED devices and as fluorescent bio-sensory materials.

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Notes and references

† *NMR and elemental analyses data* for polymers I and II: polymer I: δ(300 MHz, CDCl$_3$) 7.79 (br, 2H, Ar-H), 7.66–7.60 (br, 4H, Ar-H), 7.15 (s, 2H, Ar-H), 4.09 (br, 4H, –OCH$_2$), 2.67 (br, 4H, –CH$_2$N), 2.27 (s, 12H, NCH$_3$), 2.05 (br, 4H, fluorene 9-H), 1.12–0.78 (br, 22H, –CH$_2$, –CH$_3$). Calc. for C$_{39}$H$_{54}$O$_2$N$_2$: C, 80.41; H, 9.27; N, 4.81; Br, 0 (terminal group). Found: C, 79.60; H, 8.99; N, 4.90; Br, 0%.

Polymer II: δ(300 MHz, CD$_3$OD) 7.93 (br, 2H, Ar-H), 7.70–7.64 (br, 4H, Ar-H), 7.24 (br, 2H, Ar-H), 4.56 (br, 3.2H, –OCH$_2$), 4.38 (br, 0.8H, –OCH$_2$), 3.77 (br, 3.2H, –CH$_2$N), 3.52 (br, 0.8H, –CH$_2$N), 3.42 (br, 3.2H, NC*H*$_2$CH$_3$), 3.06 (br, 12H, NCH$_3$), 2.87 (br, 4.8H, NCH$_2$C*H*$_3$), 2.16 (br, 4H, fluorene 9-H), 1.28–0.80 (br, 22H, –CH$_2$, –CH$_3$). Calc. for C$_{39}$H$_{54}$O$_2$ N$_2$·4H$_2$O·1.6C$_2$H$_5$Br (the amounts of H$_2$O and C$_2$H$_5$Br were based on TGA analysis and ^{1}H NMR): C, 61.10; H, 8.45; Br, 15.46; N, 3.38. Found: C, 60.63; H, 8.29; Br, 16.04; N, 3.52%.

‡ The quantum yields were measured using a Perkin Elmer LS 50B luminescence spectrometer with dilute solutions (A < 0.2) at room temperature.[13] Quinine sulfate solution (*ca*. 1.0×10^{-5} M) in 0.10 M H$_2$SO$_4$ (quantum yield, 55%) was used as a standard.

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