

## Novel Water-soluble Light-emitting Materials Prepared by Noncovalently Bonded Self-assembly

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Novel noncovalently connected water-soluble nanoparticles containing hydroxyl-capped polyfluorene (PFOH) and poly(acrylic acid) (PAA) were obtained and characterized. These nanoparticles were quite stable in water and no precipitate was observed after weeks. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), and laser light scattering (DLS) were used to confirm the morphology of the PFOH/PAA nanoparticles. Their optical properties were investigated and showed the similar optoelectronic properties with PFOH solid film.

In recent years, great efforts have been devoted to the conjugated polymers for the application as fluorescent chemo or biosensors.<sup>1</sup> In this field, water-soluble conjugated polymers have attracted increasing attention as good sensory materials to detect chemical or bioactive species, such as protein, DNA, and RNA.<sup>2</sup>

To be the good candidates as biosensors, water-solubility of those conjugated polymers must be realized since most of the biomolecules were dissolved in water. The first water-soluble conjugated polymer was reported in 3-substituted polythiophene<sup>3</sup> and subsequently a series of conjugated polyelectrolytes were developed, such as poly(phenylene ethylene),<sup>4</sup> poly(phenylene vinylene),<sup>5</sup> and poly(fluorene).<sup>6</sup> Their water-solubility was obtained through introducing ionic functions to their side chains. Another way to achieve water-solubility is through block copolymerization, combining the neutral conjugated polymer segments with the water-soluble polymer segments. Our group firstly reported the water-soluble conjugated-acidic and conjugated-ionic block copolymers prepared by atom-transfer radical polymerization (ATRP) with the polyfluorene-based macroinitiator.<sup>7,8</sup> In recent years, noncovalently bonded self-assembly, a facile way to produce water-soluble micelles and other nanostructure, was used to the nanotechnology.<sup>9,10</sup> For example, Yoshida et al. reported the micelle formation of nonamphiphilic diblock copolymer via noncovalently bonded cross-linking in 1,4-dioxane.<sup>10a</sup> Jiang et al. demonstrated a series of spherical micelles obtained from polyimide (PI) with carboxyl ends, a rigid polymer, and poly(4-vinylpyridine) (PVPy) in the two polymers' common solvent.<sup>9a</sup> Unlike other methods to produce water-soluble polymers mentioned above, our water-soluble materials can be obtained directly from water-insoluble polymers assisted with water-soluble polymers and do not need any more chemical modification on polymer chain except the end groups that serve as the end-capping reagent in polymerization.<sup>10</sup> As a significant advantage in a "block-copolymer-free" strategy<sup>9</sup> for preparing water-soluble nanoparticles, here we report a new approach for the preparation of water-soluble light-emitting materials self-assembled by hydrogen bonding between of polyfluorene (PF) and poly(acrylic acid) (PAA). This phenomenon can be attributed to two main factors: the rigid character of PF and the hydrogen

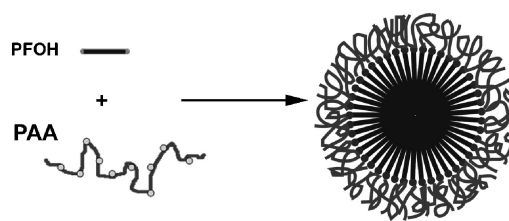
bonding between PF and PAA.<sup>9</sup>

Polyfluorenes, the high-performance blue-light-emitting polymers with great chemical and thermal stability, have attracted great interests.<sup>11</sup> Water-soluble polyfluorenes were widely investigated as the highly sensitive materials in biosensors.<sup>12</sup> Those water-soluble PFs are all obtained through attaching ionic groups on the side chains.<sup>6,8</sup> However, as far as we known, using noncovalently (hydrogen bond) connected water-soluble nanoparticles to achieve water-soluble light-emitting materials was seldom reported. In this paper, aqueous nanoparticles containing polyfluorene were successfully prepared through hydrogen bonded self-assembly between hydroxyl-capped polyfluorene and poly(acrylic acid) (Scheme 1). Their water-solubility, optical properties and morphologies were investigated and the corresponding results showed that many other types of water-soluble light-emitting materials can be conveniently and efficiently obtained by this method.

Phenylmethanol-capped polyfluorene (PFOH) was obtained by Yamamoto condensation reaction, using 4-bromobenzyl alcohol as the end-capper. The structures of the monomer and polyfluorene were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR measurements. The molecular weight of PFOH was estimated through comparing the relative integrations of total fluorene aromatic protons (from 7.66 to 7.85 ppm) and methylene protons (Ph-CH<sub>2</sub>-O, 4.78 ppm). The number-average polymerization degree of the PFOH was calculated to be about 15 (6400 g/mol). GPC measurements were also used to characterize *M<sub>n</sub>* (7010 g/mol) and *M<sub>w</sub>* (11300 g/mol) and further proved the successful synthesis of the PFOH. Poly(acrylic acid) was synthesized by radical polymerization (*M<sub>n</sub>* = 1 × 10<sup>5</sup> g/mol), using PAA in H-form in our study. See details in Supporting Information.

In a typical procedure to prepare the nanoparticles, 2 mL of H<sub>2</sub>O was added to 0.2 mL of PAA (10 mg/mL in water) under ultrasonic for 5 min, and 0.2 mL of PFOH (0.4 mg/mL in THF) was added dropwise. The resulted nanoparticles were characterized by DLS (Table 1).

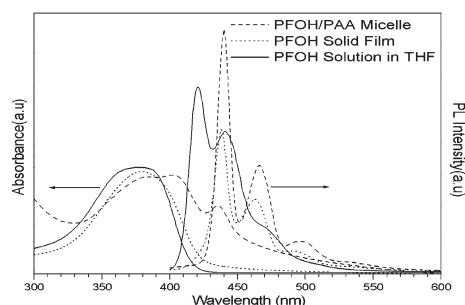
The UV-vis absorption and photoluminescence emission spectra of PFOH solution (in THF), PFOH solid film, and PFOH/PAA nanoparticles (solution in water) were shown in Figure 1. The solid film emission spectra were collected from



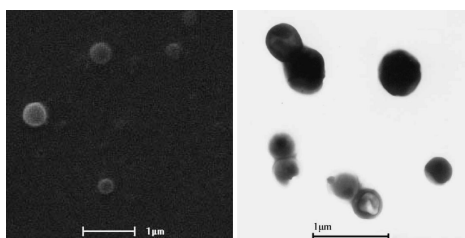
**Scheme 1.** A schematic illustration of the formation of PAA/PFOH nanoparticles.

**Table 1.** DLS characterization data of the nanoparticles and the proportion of PFOH and PAA

Sample	Diameter /nm	Polydispersity Index (PI)	PAA:PF (weight ratio, in water)
M1	283.1	0.30	25:1
M2	236.4	0.26	100:1
M3	332.5	0.40	50:1

**Figure 1.** UV-vis absorption and photoluminescence spectra of PFOH solution (1 mg/mL in THF), PFOH solid film and PFOH/PAA nanoparticle (sample M2).

solid film made by spin-coating PFOH (5 mg/mL) from THF solutions on the glass substrate. The absorption maximum of PFOH in THF solution was at 375 nm and the emission peak was at 420 nm. The absorption maxima of PFOH solid film and PFOH/PAA nanoparticle red-shifted from 375 nm (PFOH in THF solution) to 380 and 402 nm, respectively. Their photoluminescence spectra were similar and both red-shifted from 420 nm to about 440 nm, compared with the PL spectrum of PFOH in THF solution. The red-shift can be attributed to the formation of interchain  $\pi$  aggregation of PFOH.<sup>7,8</sup> The emission peak of the nanoparticles a little more red-shifted than that of the PFOH solid film (from 438 to 440 nm), which may be attributed to the more regular arrangement of PF chains in the nanoparticles.<sup>7,8</sup>

**Figure 2.** SEM (left) and TEM (right) images of nanoparticles from PFOH/PAA mixture (sample M2).

A bluish tinge appeared in the sample preparation indicated the formation of the nanoparticles and blue light under UV lamp 365 nm irradiation emitted by the mixture also proved the homogeneous dispersion of PFOH in water. In addition, the obtained pellucid PFOH/PAA solution was quite stable to water and no precipitate was observed weeks after the preparation. On the other hand, precipitate occurs immediately when directly adding the PFOH in THF solution into pure water and the similar phenomenon was observed when adding unmodified PF solution into the PAA solution (in water). These phenomena confirmed the existence of the interaction between PFOH and PAA through hydro-

gen bond. TEM and SEM observations demonstrated the morphology of the nanoparticles (diameter ranged from 100–400 nm mainly in the range 300–400 nm) obtained by the process mentioned above and gave the direct evidence of the nanoparticle aggregates. The DLS data about the nanoparticles in solutions also confirmed the results.

In summary, novel water-soluble light-emitting nanoparticles consisting of PFOH and PAA were successfully prepared by noncovalently bonded self-assembly. TEM, SEM, and DLS were used to confirm the morphology of the PFOH/PAA nanoparticles. The nanoparticles exhibit the similar optoelectronic properties to PFOH solid film. Such a noncovalently bonded self-assembly provides a novel and simple way to obtain water-soluble light-emitting materials and realize biomodification on conjugated polymers, which open opportunities for greatly improved conjugated-polymer-based biosensors. Further studies of the materials as biosensor are in progress in our laboratory.

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