

# A Novel Approach to Synthesizing Fluorescent $\pi$ -Conjugated Polymer Nanoparticles based on Ion-Association

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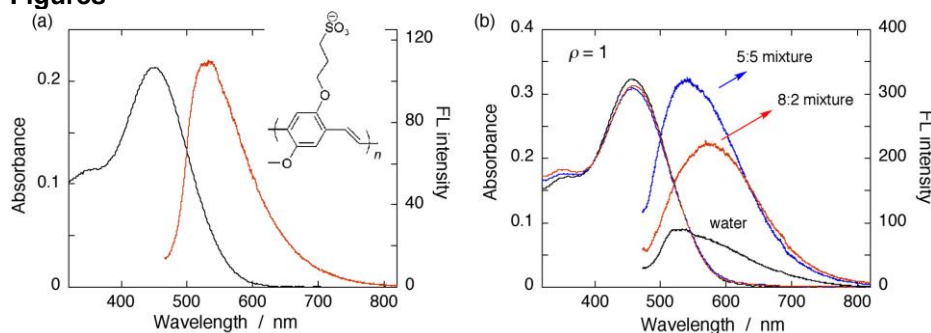
Highly fluorescent nanoparticles have been demonstrated in a wide range of applications such as high-throughput screening, live cell imaging, and intracellular dynamics. Currently available fluorescent nanoparticles include semiconductor quantum dots such as CdSe and dye-doped silica/polymer colloids. These nanoparticles are able to possess high brightness as compared to conventional fluorescent dyes. However, cytotoxicity is a critical problem for the heavy metal-containing quantum dots. There are also a number of limitations with the dye-loaded beads; for example, they have relatively large size and limited dye-loading content due to self-quenching. An unexplored alternative is the use of  $\pi$ -conjugated polymer nanoparticles as fluorescent labels, so there is growing interest in the synthesis and applications. An emulsion and/or reprecipitation method was recently developed to prepare the polymer nanoparticles with a diameter of  $\sim 30$  nm or higher that consist of hundreds of polymer molecules [1].

In the present study, we demonstrate a new method for obtaining fluorescent  $\pi$ -conjugated polymer nanoparticles based on ion association between polyelectrolytes. The "ion association method" utilizes the formation of water-insoluble ion-pair aggregates (here, polyion complexes) in aqueous phases by association of a chromophoric ion with a photochemically inert counterion to fabricate organic nano-architectures. We here chose poly(2-methoxy-5-propyloxysulfonate phenylene vinylene; MPS-PPV) as an anionic conjugated polymer (20–400 monomer repeat units per chain). Fig. 1a shows absorption and fluorescence spectra of MPS-PPV in water, and the peaks are found at 450 and  $\sim 530$  nm, respectively. Positively charged PDDA (poly(diallyldimethylammonium; average Mw =  $1\sim 2 \times 10^5$ ) was chosen as an ion-associable countercation. MPS-PPV nanoparticles were then prepared as follows: Typically, rapid addition of aqueous MPS-PPV solution (0.5 mL, 0.1 wt%) containing PDDA (0.13 mL, 0.2 wt%) into 2-propanol/water (Pro/W) mixture produced almost clear suspension of MPS-PPV-based nanoparticles, which could be confirmed by strong Tyndall scattering. In the synthesis, the monomer ratio of  $\rho = [\text{PDDA}^+]/[\text{MPS-PPV}^-]$  was controlled ( $\rho = 1$  or 8). We first examined the effect of PDDA (at  $\rho = 1$ ) on the spectroscopic properties of MPS-PPV in water. Addition of PDDA brought about a slight red shift of the absorption peak and a weak appearance of the red component ( $\sim 570$  nm) in the fluorescence. The complexation between the polymer and PDDA can be driven by their Coulombic attraction, resulting in changes in their spectroscopic properties. Next, upon adding the aqueous MPS-PPV-PDDA solution in the Pro/W mixture, interestingly, the fluorescence properties changed dramatically, although absorption spectra were almost unchanged (Fig. 1b). The invariance of absorption spectra suggests that of the effective conjugation length in the ground state. On the other hand, overall increase in the fluorescence intensity can be due to a strong motional restriction of chromophores in the polymer chains, which suppresses the nonradiative processes. Importantly, the fluorescence decrease in the blue region ( $\sim 540$  nm) as a function of 2-propanol content in the mixed solvent means an occurrence of excitation energy transfer from a shorter conjugation chromophore to a longer unit; that is, the larger the amount of 2-propanol is, the more efficient the excitation energy transfer occurs. This indicates that the MPS-PPV chain conformation in the ion-based nanoparticles is strongly dependent on the dispersion medium.

## References

- [1] (a) T. Kietzke, D. Neher, K. Landfester, R. Montenegro, R. Guntner, U. Scherf, *Nat. Mater.* **2** (2003) 408;  
(b) N. Kurokawa, H. Yoshikawa, N. Hirota, K. Hyodo, H. Masuhara, *ChemPhysChem.* **5** (2004) 1609.

## Figures



**Fig. 1** (a) Absorption and fluorescence spectra of MPS-PPV in water. (b) Absorption and fluorescence spectra of MPS-PPV nanoparticles synthesized on the basis of ion association in water and in mixed Pro/W solvents (5:5 and 8:2).