

## Enhanced photoluminescence from poly(phenylene vinylene) : dendrimer polyelectrolyte assemblies in solution†

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**Poly(2,5-methoxy-propyloxy sulfonate phenylene vinylene) (MPS-PPV) and DAB-Am-16, a generation 3.0 polypropylenimine hexadecamine dendrimer (DAB), are shown to form a tunable photoresponsive polyelectrolyte assembly in aqueous solution with an enhanced emission signal of up to 18-times that of MPS-PPV alone.**

Conjugated polymers have optical and electronic properties that are utilized in chemical and biological sensors,<sup>1,2</sup> light-emitting displays, lasers and solar cells.<sup>3</sup> Water soluble conjugated polymers (conjugated polyelectrolytes) are of particular interest for applications in chemical and biological detection.<sup>4,5</sup> However, there are several disadvantages to currently available water soluble polymers, such as low intrinsic photoluminescence (PL) quantum efficiency<sup>6</sup> and PL quenching through non-specific interactions.<sup>7</sup> In some cases, synthetic manipulations can be used to address these issues,<sup>1</sup> but such procedures are often complex and time-consuming.

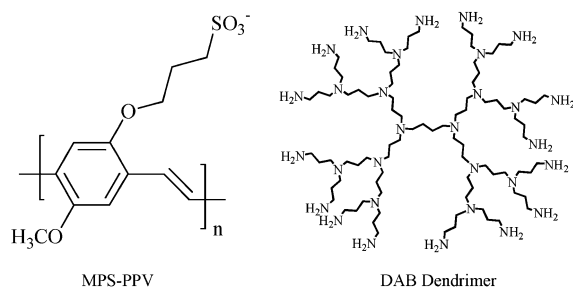
Recently, a simple method to enhance the PL quantum efficiency of an anionic conjugated polyelectrolyte, poly(2,5-methoxy-propyloxy sulfonate phenylene vinylene) (abbreviated MPS-PPV throughout; Fig. 1), was developed by adding small amounts of a cationic surfactant.<sup>8</sup> The cationic surfactants interact with the MPS-PPV, presumably forming a 'wrapped' assembly where the hydrocarbon chain of the surfactant may lie parallel to the polymer backbone, thereby forcing the polymer chain into a more linear, less coiled geometry.<sup>9</sup> The conjugated polymer-surfactant assembly was also susceptible to quenching by neutral species, which have little effect on the polymer PL alone, expanding the potential sensory uses of this material.<sup>8-10</sup> Similar photoluminescence and sensing properties have also been observed for conjugated polymer-polyelectrolyte assemblies in aqueous solutions.<sup>6,11</sup>

Motivated by the promise of polyelectrolyte assemblies for sensing devices and other applications, we have examined the detailed photophysical properties of a conjugated polymer-polyelectrolyte assembly in aqueous solution. We report a conjugated polymer-polyelectrolyte assembly with dramatically enhanced and tunable luminescent properties compared to the conjugated polymer alone. Specifically, MPS-PPV was combined

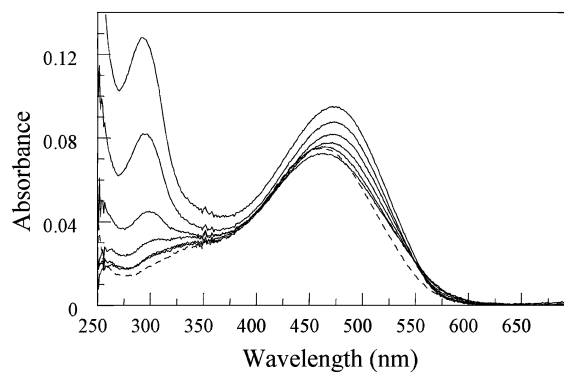
with DAB-Am-16, a generation 3.0 polypropylenimine hexadecamine dendrimer (abbreviated DAB throughout; Fig. 1), in an aqueous solution to form a photoresponsive polyelectrolyte assembly. The PL of the assembly was systematically studied as a function of DAB concentration and was found to increase to at least 18 times that of MPS-PPV alone. Since the quantum yield of fluorescence for MPS-PPV in water has been reported to be 0.02,<sup>6</sup> our results can be explained as a straightforward increase in PL quantum yield with added DAB.

Conjugated polymer-polyelectrolyte assemblies of DAB and MPS-PPV were prepared in aqueous solutions and characterized by absorption (Fig. 2) and fluorescence (Fig. 3) spectroscopies. MPS-PPV (~1000 repeat units) was prepared based on a reaction in previously published accounts,<sup>12</sup> while DAB was purchased commercially (Aldrich) and used without further purification. As seen in Fig. 2, the UV-Vis spectrum of MPS-PPV (0.005 mM in repeat units; dashed line) has a major absorption maximum at 462 nm due to transitions within the conjugated pi-orbital system. This absorption maximum was observed to red-shift ~4–5 nm upon addition of one dendrimer per repeat unit of MPS-PPV, 0.005 mM DAB. An additional increase in the DAB concentration to 0.50 mM, which corresponds to a DAB : MPS-PPV repeat unit ratio of 100 : 1, shifts the absorption maximum to 474 nm, after which increasing the concentration of DAB causes no further shift. There is, however, an increase in the absorption at 474 nm upon additionally increasing DAB concentration that is not believed to be due to contributions from overlapping DAB absorptions (note: an absorption peak at 295 nm can be used to follow the increasing concentration of DAB). The overall changes in absorption can also be observed in the difference absorption spectra (see supporting data). The magnitude of the observed red-shift for the polyelectrolyte assembly is consistent with shifts reported previously for self-assembled thin film superlattices of MPS-PPV and DAB,<sup>13</sup> which indicates that similar architectures may exist in solution and in thin film polyelectrolyte assemblies.

The fluorescence emission of MPS-PPV also undergoes dramatic changes upon complexation with DAB. In the absence of DAB, MPS-PPV has an emission maximum centered at 492 nm when

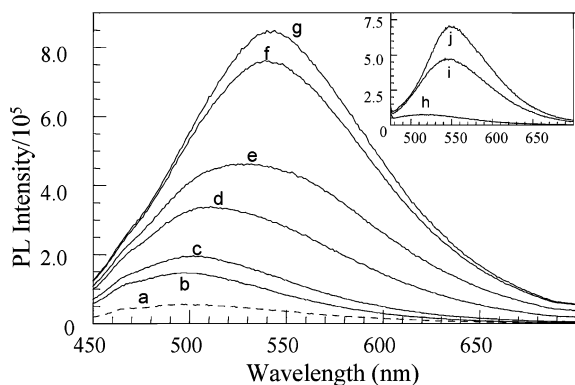


**Fig. 1** Chemical structures of the poly(2,5-methoxy-propyloxy sulfonate phenylene vinylene) (MPS-PPV) and DAB-Am-16, a generation 3.0 polypropylenimine hexadecamine dendrimer (DAB). Depending on pH, DAB is usually positively charged because of protonation of amine groups.



**Fig. 2** Absorption spectra of MPS-PPV (dashed line, 0.005 mM in repeat units) and MPS-PPV/DAB assemblies in water. Concentration of DAB in spectra shown (from bottom to top): 0.005 mM, 0.010 mM, 0.10 mM, 0.50 mM, 1.50 mM, and 2.50 mM.†

† Electronic supplementary information (ESI) available: difference absorption data. See <http://www.rsc.org/suppdata/cc/b4/b401682/>



**Fig. 3** PL of MPS-PPV(aq, 0.005 mM in repeat units, curve **a**) as a function of DAB concentration: (**b**) 0.005 mM, (**c**) 0.010 mM, (**d**) 0.10 mM, (**e**) 0.50 mM, (**f**) 1.50 mM and (**g**) 2.50 mM (Excitation: 400 nm). Inset shows PL from thin films spun-coated on fused silica slides from solutions of MPS-PPV (0.025 mM in repeat units)/DAB at (**h**) 0 mM, (**i**) 0.20 mM and (**j**) 1.0 mM DAB concentrations (Excitation: 450 nm).

excited at 400 nm, as seen in Fig. 3 (curve **a**). Upon addition of one dendrimer per repeat unit of MPS-PPV, 0.005 mM DAB, the PL emission maximum shifts to  $\sim 498$  nm and increases in intensity 3-fold. We note that, at the concentrations studied here, the polymer and dendrimer should be allowed to interact for approximately two hours, to allow the PL to stabilize. During this interaction time, the PL is observed to first significantly increase, and subsequently to stabilize, presumably reflecting the dynamics of formation of the polyelectrolyte assemblies that lead to the polymer conformational changes in solution.

As the concentration of DAB molecules per repeat unit increases, the emission maximum continues to shift towards longer wavelengths and gains intensity (Fig. 3). When there are approximately 300 dendrimers per repeat unit of MPS-PPV, 1.5 mM DAB, the PL emission reaches its maximum wavelength, 542 nm (Fig. 3, curve **e**), but still continues to gain intensity as additional DAB is added. As the ratio of dendrimer to polymer repeat unit reaches 500 to 1 the emission intensity reaches a level 18 times that of MPS-PPV alone (Fig. 3, curve **g**). Further increases with even higher concentrations of DAB are observed, but systematic studies become limited by approaching the solubility limit of DAB. We interpret the red-shift in the emission spectra of the MPS-PPV/DAB assembly as being due to an extension in MPS-PPV conjugation, while the increase in PL intensity from MPS-PPV can be explained by loss of intra- and inter-polymer quenching upon formation of the polyelectrolyte assembly. We also note that the PL enhancement for the MPS-PPV/DAB polyelectrolyte assembly is as much or greater than reports for similar MPS-PPV-surfactant assemblies.<sup>8</sup> Further, we and others<sup>6</sup> have observed varying degrees of PL enhancement and tunable PL from MPS-PPV : polyelectrolyte assemblies involving other polyelectrolytes. These data indicate that size, as well as charge density, has significant effects on the photophysical properties of the

polyelectrolyte assembly, but also suggest that enhanced/tunable PL of MPS-PPV can be achieved with a variety of species in addition to DAB.

In addition to the solution results presented above, similar enhancements and red-shifts in MPS-PPV photoluminescence were observed from thin films of MPS-PPV : DAB. Thin films were prepared by spin-coating solutions of MPS-PPV : DAB at different mol ratios onto fused silica slides. The emission spectra from such films, as well as from a thin film of MPS-PPV alone, are shown in the inset of Fig. 3. Increasing the DAB concentration in the initial aqueous solution yields an increase and red shift in PPV photoluminescence, which is similar to that observed for the solution polyelectrolyte assemblies. Thus, the PL of thin films can also be controlled by the ratio of MPS-PPV to DAB in the precursor solutions used to deposit the thin films.

In summary, we have studied the photophysical properties of a conjugated polymer-polyelectrolyte assembly, and demonstrated a tunable enhancement of the PL emission from the conjugated polymer both in solution and in thin films. Analyzing the results reported here and in the literature,<sup>8,9,11-13</sup> we conclude that the photophysical properties of conjugated polyelectrolytes can be generally controlled by modifying the type and concentration of an additional electrolytic species. These results provide improved insight into control of the photoluminescence from polyelectrolyte assemblies in solution and thin films and may lead to new strategies for developing sensors and devices that utilize the optical and electronic properties of conjugated polyelectrolytes.

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