PNIPAM-Polythiophene Microgels for Nitro Aromatic Compound Detection
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In this work we present a facile and reproducible method to obtain thermally-responsive, monodisperse, fluorescent microgels with diameters smaller than 700 nm based on poly(N-isopropyl acrylamide) (PNIPAM) interpenetrated with poly(thiophene-ethyl buthyl sulfonate) (PTEBS). Changing the temperature and inducing the microgel volume phase transition it is possible to modify the photoluminescence (PL) properties of the microgels. Thus, when the temperature was under the low critical solution temperature (LCST) of PNIPAM, PL intensity was higher than above the LCST.

Figure 1. Emission spectra of PTEBS and microgels at different temperatures (green line 25°C, blue line 35°C and red line 45°C) measured at 0.02% (w/w) concentration: A) pure PTEBS at concentration 4.3·10⁻⁴M; B) PTEBS-PNIPAM microgels with 2.5% cross-linker; C) PTEBS-PNIPAM microgels with 5% cross-linker, and D) PTEBS-PNIPAM microgels with 10% cross-linker. The inset on the right, shows a fluorescent microgels dispersion under UV illumination.

Time-resolved fluorescence measurements indicate that, in the swollen state, the increment of cross-linking increases the fluorescence decay time of PTEBS. By contrast, in the collapsed state, variations in the decay time were attributed to higher rigidity of the PNIPAM-PTEBS system, which was confirmed by neutron scattering measurements. Moreover, the shift in the wavelength of the fluorescence emission peak observed above the LCST indicates that the collapsed PNIPAM matrix was able to interact with the PTEBS chains hindering the formation of π-π interactions. This property is envisaged for developing picric acid microsensor based on the formation of π-π interactions with the π-conjugated polymer, thus quenching its PL emission. Above the LCST of PNIPAM-PTEBS microgels the interactions would be broken and the initial PL emission would be recovered.

Figure 2. a) Stern-Volmer plot for PL quenching with picric acid at 25°C (red line) and 45°C (black line). The upper inset shows the PL emission of PTEBS-PNIPAM microgels at different concentrations of picric acid at 25°C, while the inset on the bottom depicts the PL emission at 45°C for different concentrations of picric acid. b) PL intensity measured during repeated cycles of quencher addition and subsequent recovering of collapsed microgels.

In conclusion, we show an easy way for the synthesis of fluorescence microgels based on PNIPAM-PTEBS. The PL properties of the interpenetrated microgels were studied as a function of cross-linking degree, temperature, and rigidity of the polymer matrix. The results confirmed the close relationship between the environment and the PL emission of the encapsulated π-conjugated polymer. In addition, it has been developed a novel and reusable sensor for detecting nitro aromatic compounds.