

ELECTRONIC SUPPLEMENTARY INFORMATION

Photoinduced electron transfer in multilayer films composed of conjugated polyelectrolyte and amphiphilic copolymer hosting electron acceptor molecules

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P3TOSNa emission spectra at different pH

The maximum of the fluorescence spectrum of P3TOSNa at neutral pH was found at 585 nm (see Fig. S1). Upon addition of hydrochloric acid the polymer becomes self-doped, switching into more conductive and oxidized form that exhibits weaker fluorescence. In its fully oxidized form P3TOSNa's emission maximum is blue-shifted to 555 nm. Upon increasing pH the emission maximum shifts gradually (see Fig. S2) toward longer wavelength reaching 600 nm for fully reduced form (see Fig. S1) and the process is thoroughly reversible. Similar red shift of the spectrum may be observed, upon addition of a reducing agent (e. g. hydrazine).

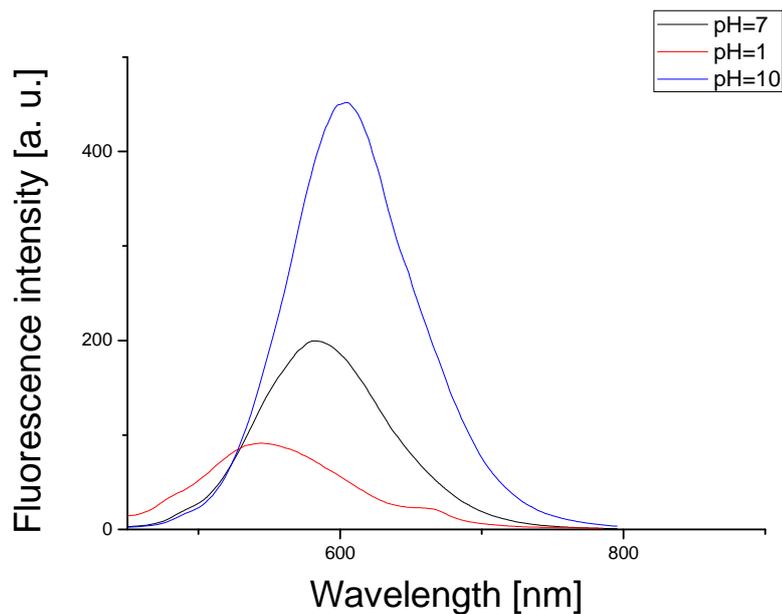


Figure S1. Emission spectra of P3TOSNa polymer ($c=0.1 \text{ g/dm}^3$) in its neutral (black line), fully oxidized (red line) and fully reduced (blue line) forms. $\lambda_{\text{ex}} = 420 \text{ nm}$.

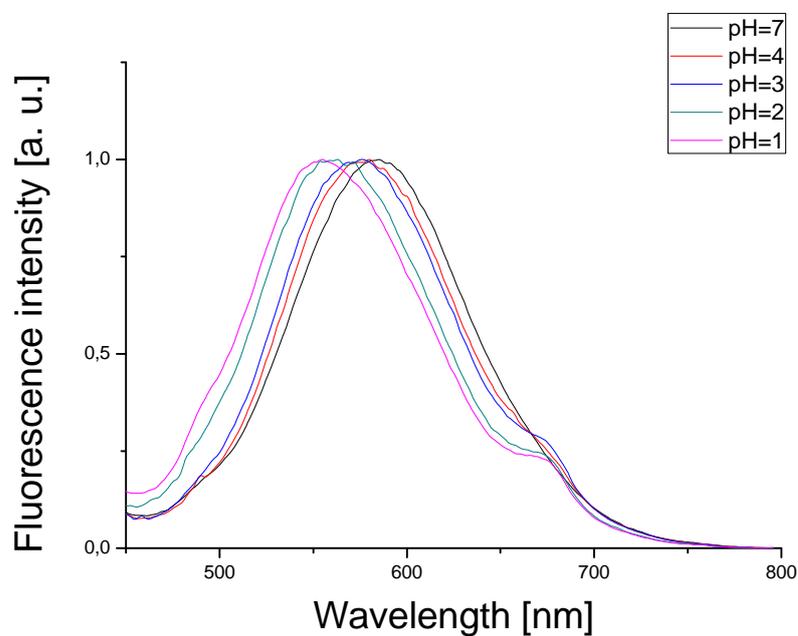


Figure S2. Normalized fluorescence spectra of P3TOSNa polymer in aqueous solutions at different pH values. $\lambda_{\text{ex}} = 420 \text{ nm}$.

P3TOSNa emission spectra in the films as a function of number of bilayers

Steady-state fluorescence emission spectra have shown 13 nm blue shift (from 585 to 572 nm) in the emission maximum for [Ak-St-H/P3TOSNa]₂ film as compared to the emission of P3TOSNa in aqueous solution (Fig. S3). That shift decreases subsequently with increasing number of bilayers (Fig. S3 inset). For 8 bilayers-thick film no shift was observed. Neutral pH of all solutions was kept throughout the deposition cycle.

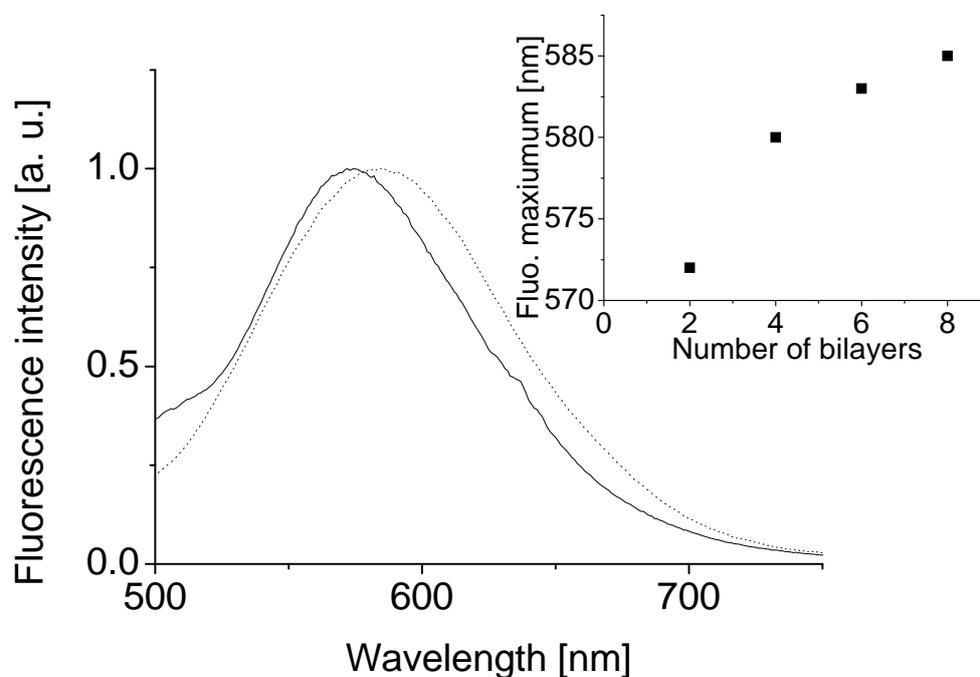


Figure S3. Normalized fluorescence emission spectra of [Ak-St-H/P3TOSNa]₂ film (solid line) and P3TOSNa solution (dot line); $\lambda_{\text{ex}} = 420$ nm. Inset: the films' emission maxima as a function of number of bilayers.

AFM imaging of [PDADMAC/P3TOSNa]₂ LbL film.

The LbL film containing linear homopolymer, poly(diallyldimethylammonium chloride) (PDADMAC) instead of Ak-St-H copolymer was fabricated and studied by AFM (see Fig.

S4). The grain size analysis of the AFM image of [PDADMAC/P3TOSNa]₂ film revealed the features with diameters of 8-10 nm, which are smaller than the ones observed for [Ak-St-H/P3TOSNa]₂ (15-25 nm). The performed blank experiment suggests that the grains observed for the films containing Ak-St-H may be assigned to the micellar structures formed by this copolymer in solution.

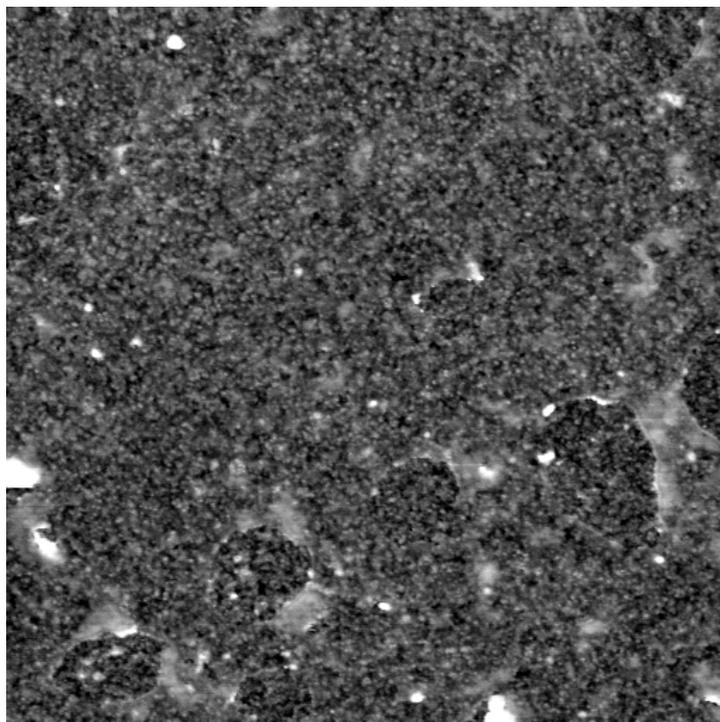


Fig. S4. AFM picture of [PDADMAC/P3TOSNa]₂ film. Image size is 2 μm x 2 μm and z-scale is 10 nm.

Amplified fluorescence quenching of P3TOSNa polymer in solution.

Fluorescence quenching experiment of P3TOSNa was performed by gradually adding 10 μl of 5 · 10⁻⁵ M aqueous solution of methyl viologen (MV²⁺) into 2 ml of the polymer solution (c = 0.1 g/dm³) and collecting fluorescence spectra (λ_{ex} = 420 nm). Using Stern-Volmer equation Stern-Volmer constant was calculated to be 7.8 · 10⁵ [M⁻¹] (see Fig. S5). Such a high value of SV constant indicates that amplified fluorescence quenching occurs in the system in solution.

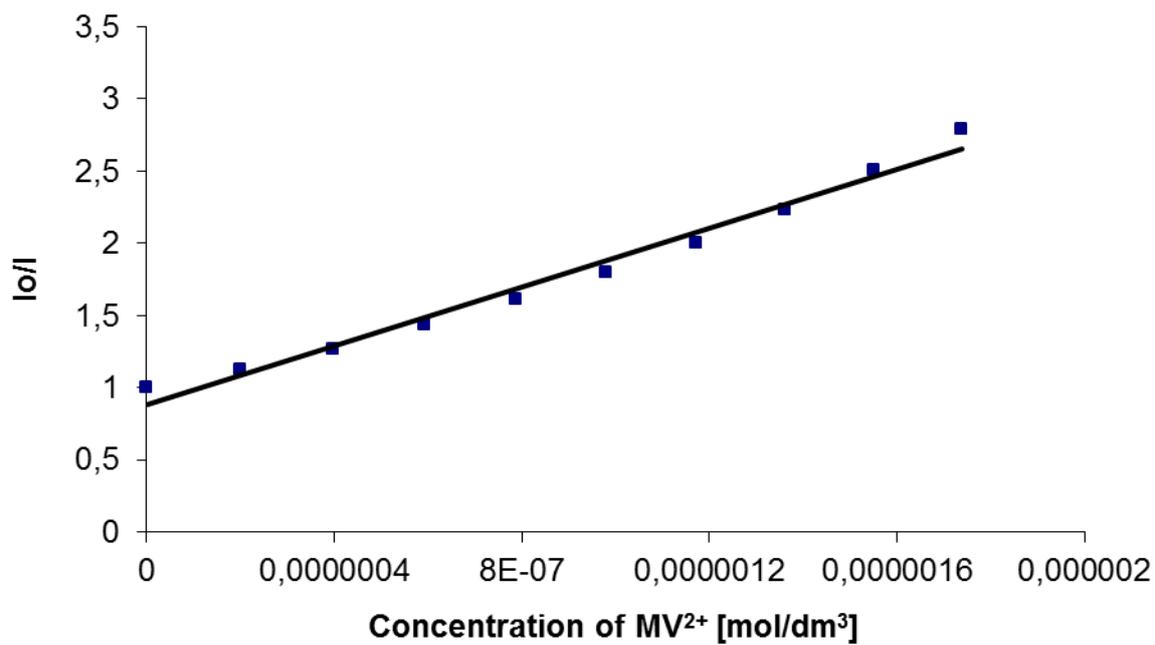


Figure S5. Stern-Volmer plot for the amplified fluorescence quenching of P3TOSNa polymer with methyl viologen.