Supporting Information

Electrofluorescence Switching from Electrochemically Convertible A Multilayer Thin Film by Layer by Layer Assembly of Anionic Fluorescent Conjugated Polyelectrolyte with Poly(diallyldimethylammonium chloride)

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Contrast experiments for the switching rate study, using PFTU as a standard for comparison

Fabrication of a PFTU EF device. The electrofluorescent film was prepared by spin-coating (5000 rpm, 60 s) a solution of PFTU (10 mg mL\(^{-1}\) in CHCl\(_3\)) onto an ITO-coated glass substrate and dried under vacuum at 80°C for 5 min. In our study, this layer also possessed a switching mechanism as well as photoluminescence. Another layer of the gel electrolyte prepared from PPC (1.0 g), LiClO\(_4\) (0.15 g) and PC (3.0 g), and heated at 60 °C to obtain a homogeneous and transparent gel, was spread on top. The device was then sandwiched with another piece of ITO electrode and sealed with epoxy resin.

To further understand the EFD behavior of \((\text{PFTSO}_3\text{Na}/\text{PDDA})_n\), an EFD based on PFTU (Scheme S1), our previously reported EFD polymer, was fabricated under the same conditions for comparison. The thickness of 70±5 nm for the PFTU was measured by an alpha-step instrument. This value is slightly larger than that of 43±5 nm for \((\text{PFTSO}_3\text{Na}/\text{PDDA})_{20}\) but still in the same order of magnitude.

Scheme S1. Structural formula of PFTU.

Figure S9 shows the results from the contrast PFTU device. The device showed an
on-to-off switching time of 3.53 s at 1.0 V and an off-to-on switching time of 6.06 s at -1.0 V. Although the on-to-off switching times for the (PFTSO$_3$Na/PDDA)$_{20}$ and PFTU EFDs are very similar, the off-to-on switching time of 6.06 s for the PFTU EFD is obviously much slower than that of 1.88 s for (PFTSO$_3$Na/PDDA)$_{20}$. Furthermore, their fluorescence resumption profiles are very different; an induction period of 5 seconds was undoubtedly observed for PFTU. On the contrary, the induction period has not been observed for (PFTSO$_3$Na/PDDA)$_{20}$ in Figure 10b. This result suggests that the interpenetrating PFTSO$_3$Na/PDDA polymer network not only shows high conductivity for the TAA radical cations and the bications but also allows the ClO$_4^-$ counter-anions to migrate and effectively diffuse back to the gel-electrolyte under the applied reverse bias of -1.0 V during the off-to-on (de-doped) process.

**Figure S9.** Electrofluorescence switching time profile of the PFTU device at 435 nm with the electrical voltage bias of ±1.0 V.