Electronic Supplementary Information

Photoluminescence from poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) in the visible region

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Absorption and photoluminescence spectra, map of photoluminescence excitation, and time evolution of photoluminescence from the other PEDOT/PSS films

The PEDOT/PSS was obtained from Sigma-Aldrich Co. (high-conductivity grade, 1.3–1.7% in H_2O, henceforth called PEDOT/PSS(high)) and used as purchased. The carrier density of the PEDOT/PSS(high) was measured to be 1.8×10^{20} cm^{-3} by employing THz time-domain spectroscopy [S1]. Film samples for absorption measurements were fabricated by spin-coating the solutions on CaF_2 substrates. For PL measurements of PEDOT/PSS(high), freestanding films were prepared by drop-casting the solution on glass substrates and then removing the films from the substrates after drying under ambient conditions.

Figure S1 shows the absorption and photoluminescence (PL) spectrum for the PEDOT/PSS(high) film. The ratios of the absorption coefficient at 4.7 eV (PSS) to those at 0.5 and 1.5 eV (PEDOT) are 0.3 and 1.0, which are smaller than in the PEDOT/PSS (low-conductivity grade) film in the main text (the ratios are 1.4 and 3.2). The weight ratio of PSS to PEDOT in PEDOT/PSS(high) is estimated to be 4–6 by using that in PEDOT/PSS in the main text (19 ~ 2.6/0.14) and the above ratios of the absorption coefficient. (This is rough estimation because the doping level of PEDOT is different between the two samples and the strengths of polaron absorption bands in the two samples are different.) Thus, in the PL measurements, the number of photons absorbed by PSS in the PEDOT/PSS(high) film is much smaller than that in the PEDOT/PSS film in the main text. Indeed, the PL intensity of PSS is about ten times weaker in the PEDOT/PSS(high) film. The map of PL excitation (PLE) in Fig. S2 also shows quite weak PL from PSS. Figure S3 shows the PL decay curve, which is fitted by a triple-exponential function model, $\propto \alpha_1 \exp(-t/\tau_1^{a}) + \alpha_2 \exp(-t/\tau_2^{a}) + (1-\alpha_1-\alpha_2)\exp(-t/\tau_3^{a})$, with $\alpha_1 = 0.78$, $\alpha_2 = 0.19$, $\tau_1^{a} = 0.05$ ps, $\tau_2^{a} = 0.29$ ps and $\tau_3^{a} = 4.50$ ps. The value of the ratio, $(\alpha_2\tau_2^{a} + (1-\alpha_1-\alpha_2)\tau_3^{a})/\alpha_1\tau_1^{a}$ is 5. Consequently, a relatively small amount of PSS results in weak PL from the PEDOT/PSS film in the visible region.

[S1] T. Unuma, K. Fujii, H. Kishida and A. Nakamura, *Appl. Phys. Lett.*, 2010, **97**, 033308.

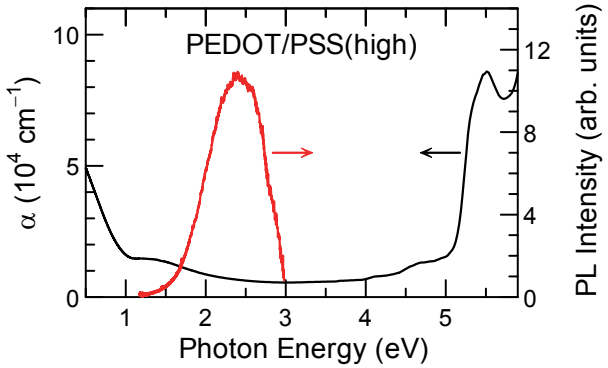

Fig. S1 Absorption and photoluminescence spectra of PEDOT/PSS(high).

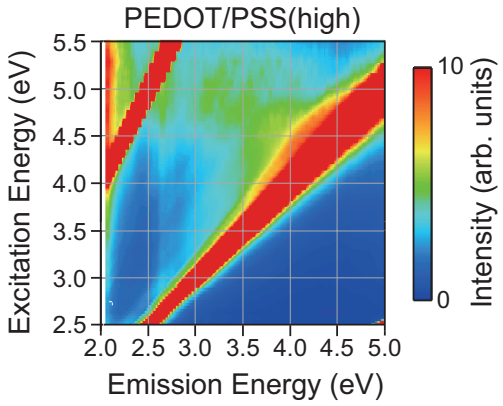

Fig. S2 Map of photoluminescence excitation spectrum of PEDOT/PSS(high). The intensities are not calibrated.

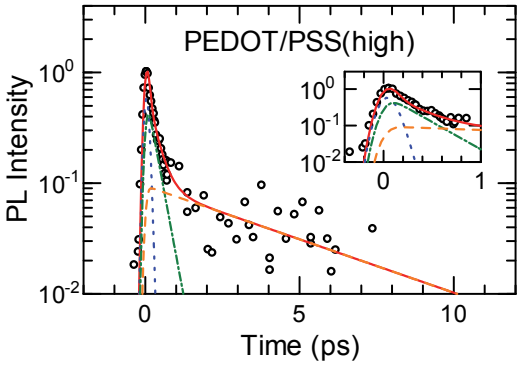

Fig. S3 Time evolution of photoluminescence intensity at 2.4 eV in PEDOT/PSS(high).