Supplementary material (ESI) for Journal of Materials Chemistry


# Supplementary Information

# β–Phase Formation in Poly(9,9-di-*n*-octylfluorene) by Incorporating Ambipolar Unit–phenothiazine and 4-(dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino)styryl]-4*H*-pyran

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**Optical Properties.**

We synthesized F8R12 (0.12 mol% ambipolar monomer) and F8R15 (0.15 mol% ambipolar monomer) by Suzuki coupling polymerization. The number-average molecular weight (*M*n) of the polymers were found to be 55,000 and 63,000 with polydispersity indices of 2.1 and 2.2 respectively. Normalized UV-vis absorption and PL emission spectra of thin films of the polymers are shown in Figure R-1 and Figure R-2 respectively.

As shown in Figure R-1, the all polymers (F8Rs) show an absorption maximum at about 395 nm, which is attributed to a $\pi$–$\pi^*$ transition of the polymer. Also, a new peak appears at 436 nm whose intensity increase upon increasing the fraction of DCM units but without any shift in position. The fact that this emerging peak does not shift in position indicates that the incorporation of the ambipolar unit results in very long and extended chain segments (i.e., the β phase) without the formation of intermediate states.

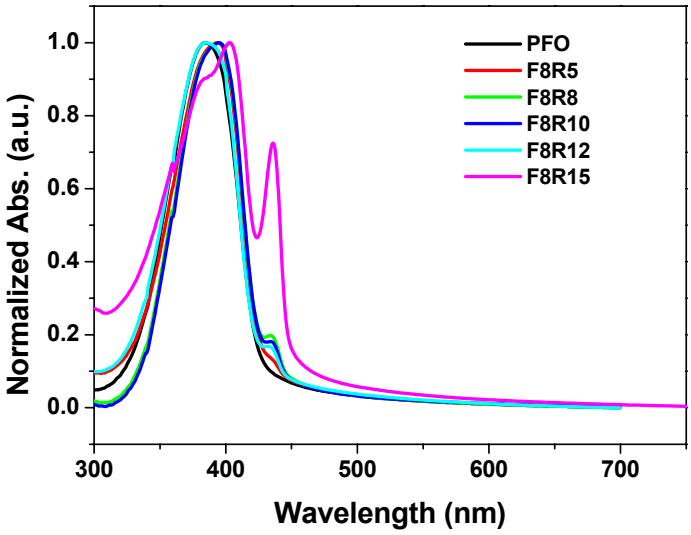


**Figure S-1. UV-vis absorption spectra of thin films of the copolymers.**

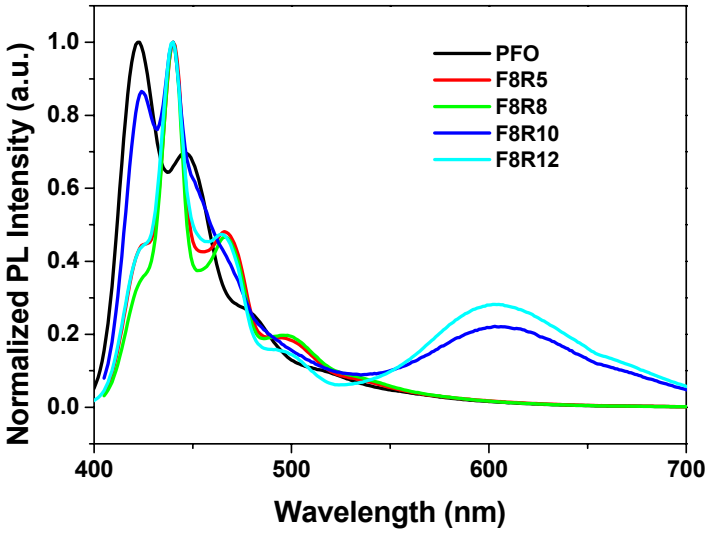


**Figure S-2. PL spectra of thin films of the copolymers.**

As shown in Figure R-2, the PL spectra of the F8Rs (excited at the main absorption wavelength of 395 nm) show characteristic bands attributed to the β phase, at 440 (0-0 band),

465 (0-1 band), and 498 nm (0-2 band), as well as an additional 0-0 band from the amorphous matrix at 424 nm. This result indicates that parts of the chains undergo an extension of the conjugating length (β phase) upon incorporating the ambipolar unit into the PF polymer system.