Supporting Information

Directed Assembly of Hierarchical Supramolecular Block Copolymers: A Strategy to Create Donor-Acceptor Charge Transfer Stacks

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1. FTIR Spectra

Figure S1. FT-IR spectra of NDI, PBA, PS-\(b\)-P4VP, PS-\(b\)-P4VP(PBA)\(_{0.5}\), and PS-\(b\)-P4VP(PBA+NDI) in the different regions (a) 1430-1400 cm\(^{-1}\) and (b) 1610-1585 cm\(^{-1}\).

2. \(^1\)H NMR spectra
Figure S2. $^1$H NMR spectra of (a) PS-$b$-P4VP (b) PBA (c) NDI (d) PS-$b$-P4VP(PBA)$_{0.5}$ (e) PS-$b$-P4VP(PBA+NDI), (f) PS-$b$-P4VP and PS-$b$-P4VP(PBA)$_{0.5}$ showing the complex formation. The $^1$H NMR spectra displaying the downfield shifts (8.21- 8.27ppm) of the two aromatic pyridine protons near to nitrogen occurs because of the hydrogen bonding between the carboxylic OH of PBA and lone pair of electrons on the nitrogen atom of pyridine (Adv. Funct. Mater. 2013, 23, 2033–2043.) and (g) $^1$H NMR spectra of NDI, PS-$b$-P4VP(PBA+NDI) and PBA displaying the up-field shifts of aromatic protons because of CT complexation (Langmuir, 2019, 35, pp 478–488).

3. TEM image

After thermal annealing and cooling of PS-$b$-P4VP(PBA+NDI), the SAXS peaks corresponding to lamellae in Figure 3a are less distinct. The formation of lamellar morphology was further confirmed by TEM as shown below. It has to be noted that, we have used PS-$b$-P4VP(PBA+NDI) solution coated TEM grids for thermal annealing.
4. Complexes with homopolymer poly(4-vinyl pyridine) (P4VP)

We investigated the role of homopolymer P4VP in stabilizing the charge transfer complexes using PBA and NDI through noncovalent interactions. The homopolymer P4VP with number-averaged molecular mass is \( M_n \): P4VP 60000 g mol\(^{-1}\) was used in this work. FTIR spectra confirmed the formation of hydrogen bonding between P4VP and PBA. Wide-angle X-ray diffraction results revealed that PBA added P4VP (P4VP(PBA)\(_{0.5}\)) supramolecules resulted in the partial aggregation of PBA as shown in Figure S4(a). In the case of the block copolymer, no such aggregation was observed PS-b-P4VP(PBA)\(_{0.5}\). With the addition of NDI to P4VP(PBA)\(_{0.5}\) complex, at room temperature P4VP(PBA+NDI) shows several crystalline reflections over the amorphous halo of P4VP as shown in Figure S4(b). Similar to block copolymer supramolecules, a new reflection was observed at \( 2\theta = 4.8^\circ \) \( (d = 1.84 \text{ nm}) \) corresponding to the hierarchical assemblies of small molecules within P4VP. Up on heating to 240 °C and cooling, the peak corresponding to the hierarchical assemblies of small molecules was reappeared along with the crystalline reflections of NDI. These results indicated that though the C-T complexes are forming in the case of homopolymer similar to the block copolymer supramolecules, however, the agglomeration of PBA and NDI are observed, which might be due to the high molecular weight of homopolymer P4VP used.
Figure S4. (a) WAXS pattern of P4VP(PBA)$_{0.5}$ and (b) Temperature-dependent WAXS patterns of P4VP(PBA+NDI).

The formation of PBA and NDI charge-transfer complexes within the homopolymers were further understood by monitoring the UV/Vis spectroscopy and solid-state photoluminescence spectrum as shown in Figure S5. In the solid state, the P4VP(PBA+NDI) shows absorption band at around 540 nm, similar to the block copolymer supramolecules (PS-$b$-P4VP(PBA+NDI)) indicating the formation of the CT complexes (alternate DA stacks) between PBA and NDI within the homopolymer chains. At the same time, the PL spectrum of P4VP(PBA+NDI) shows significant quenching of the PBA emission in the homopolymer supramolecules.

Figure S5. (a) UV/Vis spectra of P4VP(PBA+NDI) and (b) PL spectra of P4VP, P4VP(PBA)$_{0.5}$ and P4VP(PBA+NDI) in the solid state.