Figure S1. WAXS profiles of PS-b-P4VP(TOB). Note that with $x = 0.7$ and 0.2, there is no observable reflections from pure TOB crystals, indicating that TOB can disperse in the supramolecular complex well up to $x = 0.7$. 
Figure S2 FT-IR spectra for the TOB, PS-\(b\)-P4VP(TOB)\(_x\), and PS-\(b\)-P4VP, respectively.

The FT-IR spectra of the pure TOB, PS-\(b\)-P4VP and PS-\(b\)-P4VP(TOB)\(_x\), are shown in Figure S2. For pure TOB, the stretching modes of the hydroxyl groups involving the hydrogen-bonded dimers and Fermi resonances are evidenced by the 3100, 2670, and 2545 cm\(^{-1}\) bands (marked by asterisks). The absence of the TOB dimer bands together with the appearance of two new broad bands near the 2500 and 1940 cm\(^{-1}\) (marked by dotted lines), in the spectra of PS-\(b\)-P4VP(TOB)\(_x\) with different TOB contents, are attributed to the O-H stretching band and its Fermi resonances of well dispersed TOB hydrogen-bonding with P4VP. The shift of the carbonyl band of TOB at 1687 cm\(^{-1}\) to 1704 cm\(^{-1}\) (as marked by the broken line) furthermore supports the formation of hydrogen bonding between carboxylic acids of TOB and pyridines of P4VP blocks in PS-\(b\)-P4VP(TOB)\(_x\).
Figure S3  Detailed evolution of 2D SAXS patterns in situ obtained for the solvent-cast film of PS-\textit{b}-P4VP(TOB)$_{0.7}$ subject to subsequent thermal stretching and annealing: at room temperature before stretching (a), at 120 °C under low stretched ratio of ~1.2 (b), at 120 °C under higher stretched ratio of ~2 (c), cooled down to 85 °C following by releasing stress (d), at 85 °C for long annealing time of more than 6 hours (e). The arrow in (e) indicates the stretching direction.
Details of the columnar LC structure.

In the text, Figure 2f exhibits three sharp arc-like reflections along the equatorial direction with a peak position ratio 1: $3^{1/2}$: 2, revealing a corresponding local LC phase transformation (from the oriented smectic layers) to HEX$_{col}$ columns of P4VP(TOB)$_{0.7}$. These columnar domains are highly oriented in the direction perpendicular to the stretching. Moreover, the 2D WAXS pattern (inset of Figure 2f) displays a diffuse halo at $q = 13$ nm$^{-1}$ ($d = 0.48$ nm) with an emphasis on the four-lobe pattern (Figure S4 shown below). This corresponds to oriented TOB molecules, with the fan-like molecular plane (including $\pi-\pi$ stacking and the three coplanar aliphatic chains) forming a preferred inclined angle 55° with the column axis; spread of the orientation is, however, significant ($\pm \sim 20^\circ$) as shown in Figure S4.

Figure S4  Azimuthal scan for the intensity profile of the four-lobe reflection pattern observed ($q = 13$ nm$^{-1}$) in the inset of Figure 2f.

Figure S5 TEM images of microtomed sections (with iodine-stained P4VP domains in black) cut along the $XZ$ plane (a), $YZ$ plane (b) and the $XY$ plane (c), for constructing the 3D representation in Figure 4 for the HEX$_{col}$-within-TPL structure of PS-$b$-P4VP(TOB)$_{0.7}$.

Reference