Supplementary Information

Figure S1 The optical images of the spin-coated H1-BCz film on carbon-coated glass substrates when exposed to different THF vapor pressures for 16 hours. The distances between the sample position and the solvent liquid surface are (A) 0.6 cm, (B) 2.2 cm, (C) 3.8 cm, (D) 5.4 cm, (E) 7 cm and (F) 10.2 cm, respectively. (A'), (B'), (C'), (D'), (E'), (F') are the polarized images of (A), (B), (C), (D), (E), (F), respectively.

Figure S2 The images of the self-assembled H1-BCz fibers formed on carbon-coated glass substrates when exposed to different hexane vapor pressures for 16 hours. (A), (B), (C), (D) are the optical images and the distances between the sample position and the solvent liquid surface are (A) 0.6 cm, (B) 2.2 cm, (C) 3.8 cm, (D) 5.4 cm. (E), (F), (G), (H) are the relative AFM height images and (I), (J), (K), (L) are the relative TEM images of (A), (B), (C), (D). The size of the AFM height images is 10 μm×10 μm.
Figure S3 The in-situ observation of the film morphology changes of H28 films when the spin-coated film on silicon substrates exposing to a certain THF annealing vapor (The position of the sample is 1.6 cm higher than the solvent liquid surface and the volume of the pre-added solvent is 0.05 ml.) for different times. The snapshots from real-time optical microscopy taken at (A) 0 min, (B) 4 min, (C) 6 min, (D) 8 min, (E) 10 min, (F) 12 min, (G) 14 min and (H) 15 min, respectively.
**Figure S4** The optical images of the H28 films (A), (B), (C) on glass and (D), (E), (F) carbon-coated glass substrate when exposed to different hexane vapor pressures for 16 h. The distance between the sample position and the solvent liquid surface is (A) and (D) 0.6 cm, (B) and (E) 2 cm, (C) and (F) 3.8 cm.

![Figure S4](image)

**Figure S5** Concentration-dependent luminescence spectra of (A) H1-BCz and (B) H2-BCz in CH₂Cl₂. The concentrations for H2-BCz solution are 1×10⁻¹ M (black line), 2×10⁻² M (red line), 1×10⁻² M (blue line), 1×10⁻³ M (dark cyan line), 1×10⁻⁴ M (magenta line), 1×10⁻⁵ M (dark yellow line) and 1×10⁻⁶ M (navy line). The excitation wavelength is 290 nm.

![Figure S5](image)
**Figure S6** The contact angle of the solvents on the substrates: (A) THF on glass, (B) hexane on glass, (C) THF on carbon-coated glass and (D) hexane on carbon-coated glass.