Supplemental Material:

Sensitive Characterization of the Influence of Substrate Interfaces on Supported Thin Films

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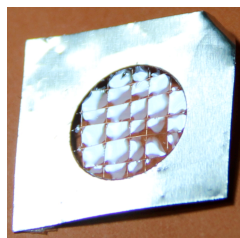
Figure S1: Optical image of ultra thin free standing film (~25nm) captured on the aluminum plate with a circular opening of 1.5 cm in diameter. The openning is filled with very fine copper wires to support the ultra thin film.
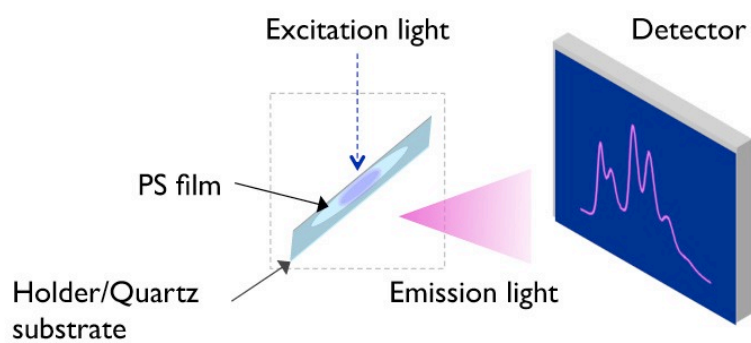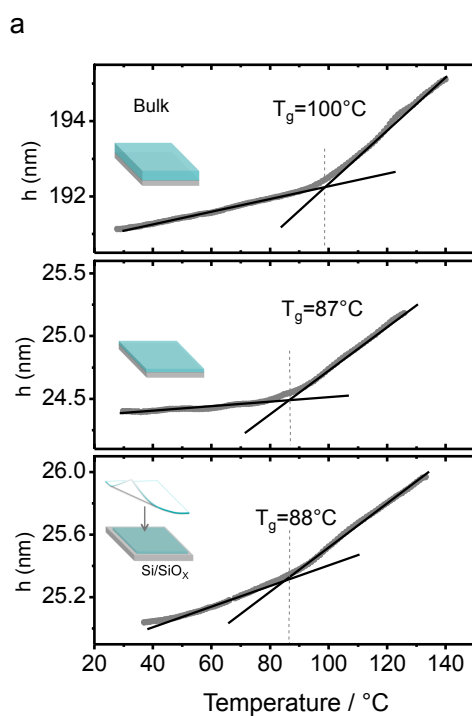

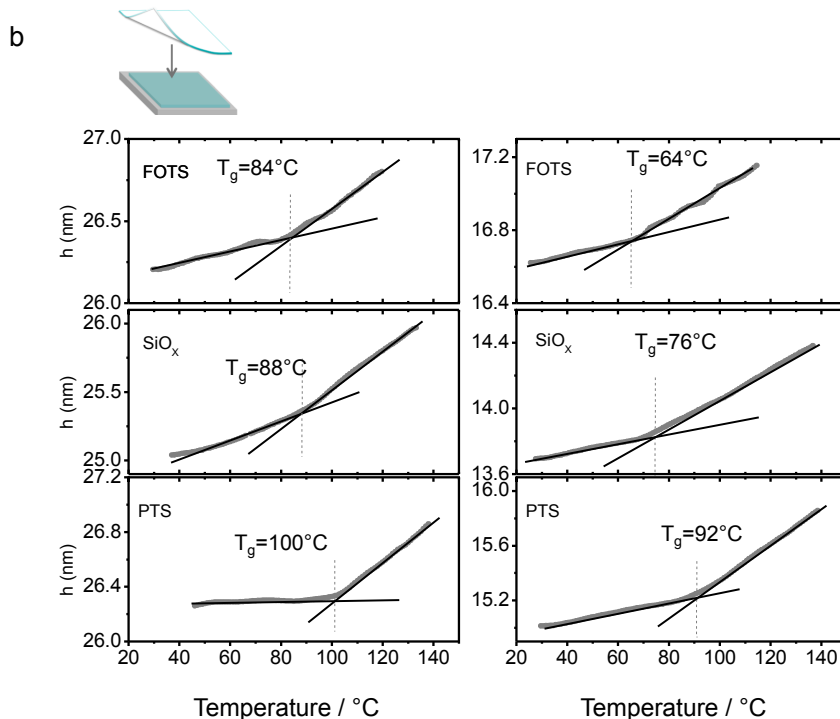**Figure S2:** Schematic of the optical pathway for fluorescence measurement.

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Figure S3 (a): The film thickness h of PS films as a function of the sample temperature T. Top: a thick film with thickness of 190nm supported on Si substrate. All the film was annealed at 120°C for 24 hours. Middle: thin film with thickness of 25nm spin coated on the Si substrate. Bottom: thin film with thickness of 25nm transferred to Si substrate after annealed. The T_gs of supported film and transferred film are nearly the same, which is consistent with the results get in Figure 3.**(b): T_g values of films supported on Si substrate with modified surfaces.** We observed that a much less T_g reduction in films on phenethyl-group modified substrate, confirming the results in Figure 4.
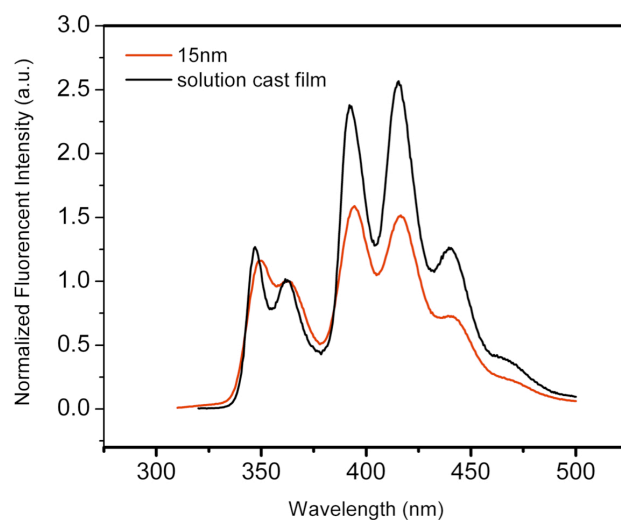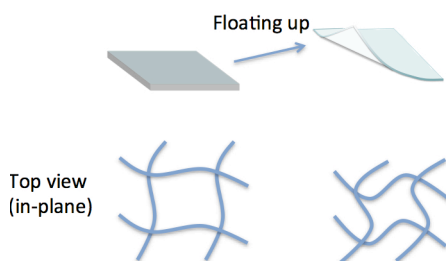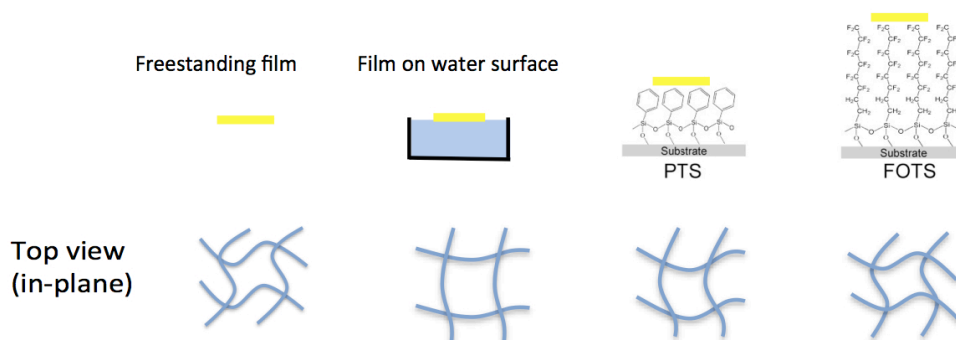
Figure S4：NRET ratio I_A/I_C for a supported thin film (red) and the bulk sample(black).

Schematic 1: a closer in-plane interchain proximity in freestanding films after removing the supported substrate.

Schematic 2: The in-plane interchain proximity in freestanding films, water surface and modified substrate (PTS and FOTS).