## **Supporting Information**

to

## Modular synthesis of poly(perylene bisimides) using click chemistry: A comparative study

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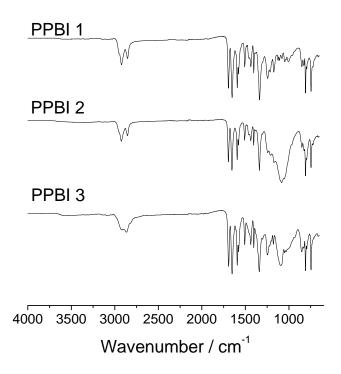


Figure S1: FTIR spectra of hydrophobic PPBIs 1-3.

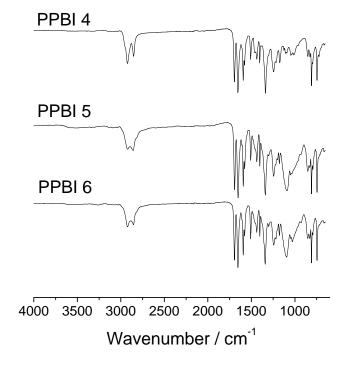
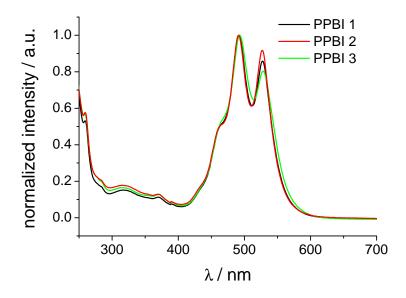


Figure S2: FTIR spectra of hydrophilic PPBIs 4-6.



**Figure S3:** Absorption spectrum of hydrophobic **PPBIs 1-3** in chloroform solution (10<sup>-5</sup> M) normalized at 490 nm peak.

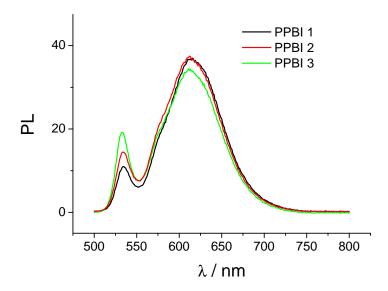
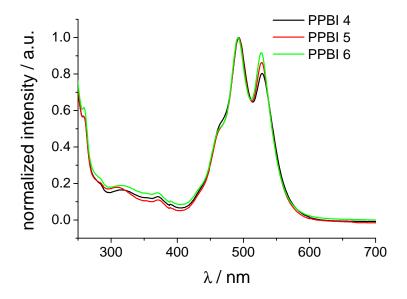


Figure S4: Photoluminescence spectra of hydrophobic PPBIs 1-3 in chloroform solution (10<sup>-5</sup> M).



**Figure S5:** Absorption spectra of hydrophilic **PPBIs 4-6** in chloroform solution ( $10^{-5}$  M) normalized at 490 nm peak.

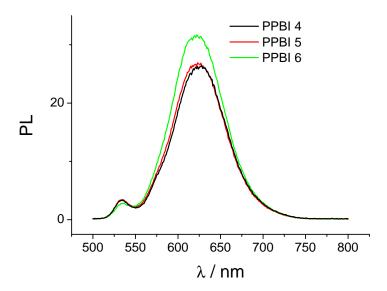
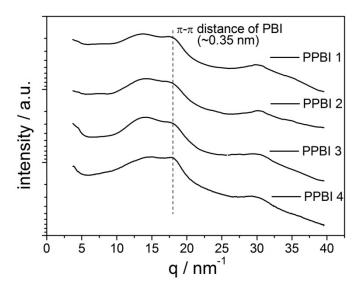
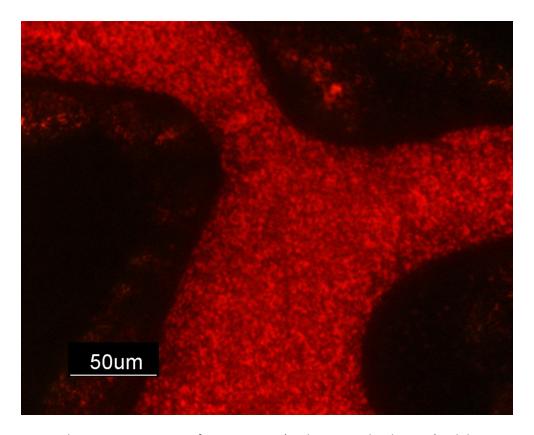


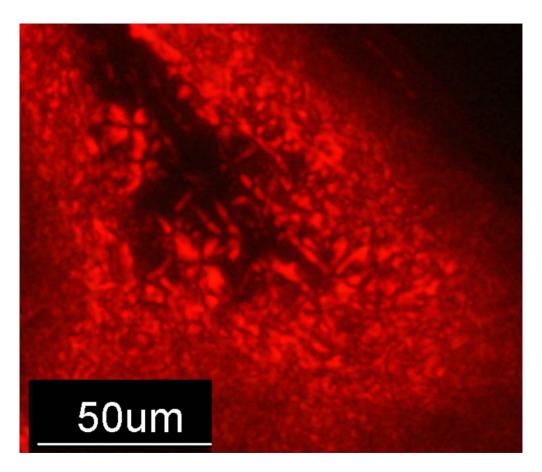
Figure S6: Photoluminescence spectra of hydrophobic PPBIs 4-6 in chloroform solution (10<sup>-5</sup> M).



**Figure S7:** WAXS data of **PPBI 1-4**. The dashed line indicates the  $\pi$ - $\pi$  distance the PBIs.



**Figure S8:** Optical microscopic image of **PPBI 1** at RT (under crossed polarizers) exhibiting LC texture, which does not change in the temperature range between 290 °C and RT. Due to a very high viscosity of side chain liquid crystalline polymers, the characteristic SmC textures could not be assigned. The film was cooled down from isotropic melt with 10K/min.



**Figure S9:** Optical microscopic image of model compound **PBI-Sty 6** at RT (under crossed polarizers). The observed texture can best be described as focal conic and did not change in the temperature range between 150 °C and RT. The film was cooled down from isotropic melt with 10K/min.

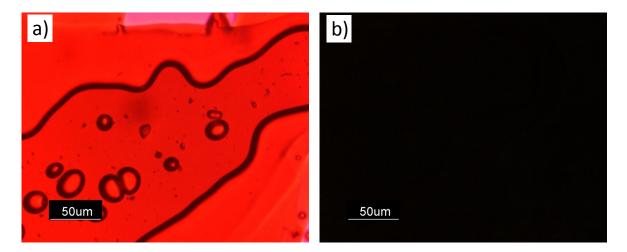


Figure S10: Optical microscopic images of polymer PPBI 2 at RT under crossed polarizers a) with and b) without a  $\lambda/4$  plate. No birefringence or LC texture could be observed. The film was cooled down from 280 °C with 10K/min. Also prolonged annealing just below the  $T_c$  and slow cooling at 1K/min resulted in no birefringence or LC texture.

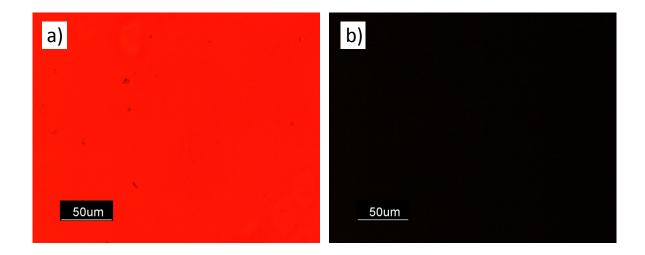


Figure S11: Optical microscopic images of amorphous polymer PPBI 4 at RT under crossed polarizers a) with and b) without a  $\lambda/4$  plate. As expected no birefringence or LC texture is observed. The film was cooled down from 250 °C with 10K/min. Also long annealing just below the  $T_c$  and cool rates of 1K/min gave no birefringence of texture.

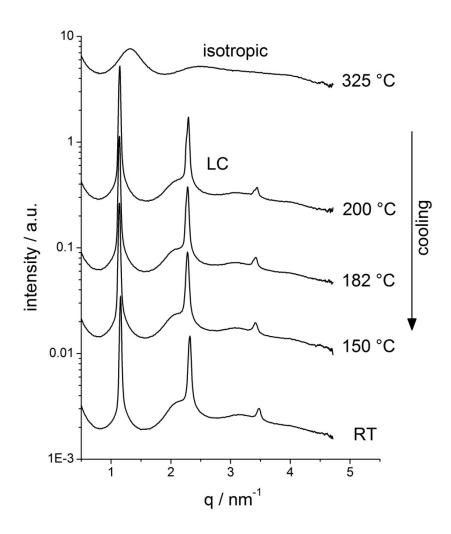


Figure S12: Temperature dependent SAXS data of PPBI 1 upon cooling from 325 °C. The liquid crystalline spectra recorded below melting point show a superposition of the broad peak due to amorphous parts and sharp reflections from the LC order.

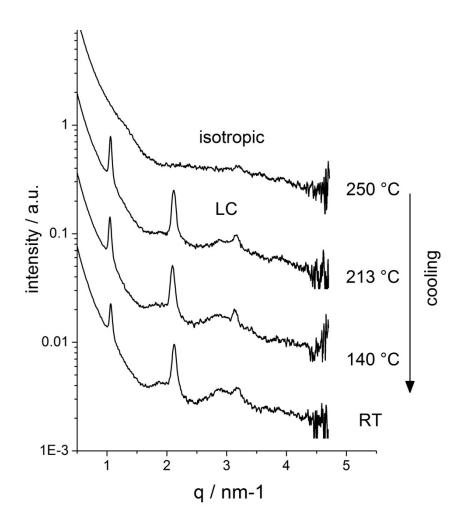
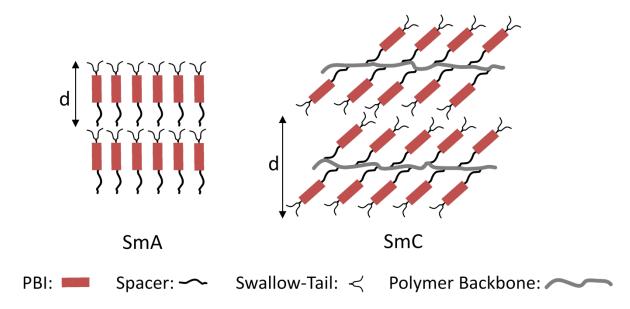


Figure S13: Temperature dependent SAXS data of PPBI 2 upon cooling from 250 °C.

Considering the fact that the length of the fully stretched PBI side group in PPBI-1 is 4.28 nm, in the case of monolayer SmA the lamella thickness would be either 8.56 nm for a non interdigitated phase or around 4.28 nm for a fully interdigitated phase. But the observed lamella thickness is 5.46 nm. An intermediate structure between the fully stretched and fully interdigitated forms is not very likely due to the disturbed space filling and decrease in extent of  $\pi$ - $\pi$  stacking among PBI units. This leads us to suggest a SmC phase with tilted mesogens for **PPBI 1** and **PPBI 2**.



**Figure S14**: SmA phase packing for the model compound **PBI-Sty 6** and a possible SmC structure for the polymers **PPBI 1** and **PPBI 2**. The tilt angle in SmC depends on the degree of interdigitation/mixing up of the swallow tail substituents.