



Amphiphilic, All-Conjugated Block Copolymers

Synthesis and Solvent-selective Photoluminescence Quenching

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Introduction:

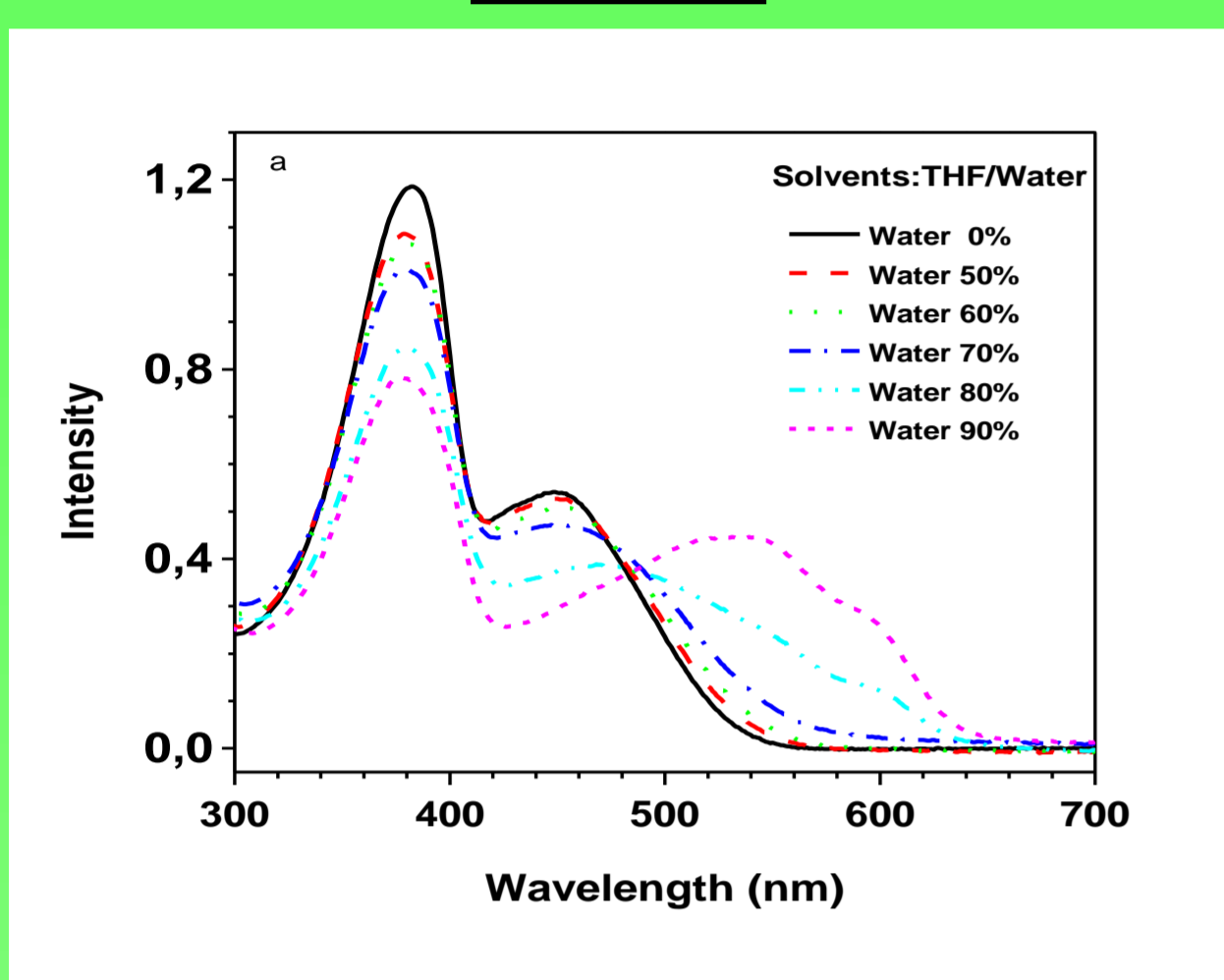
Block copolymers and their supramolecular structure formation have attracted particular attention due to potential applications in nanotechnology, micro reactors, membrane transport, and biochemistry. For coil-coil diblock copolymers, the observed nanostructure formation is mainly driven by nanophase separation. Hereby, the dominating role of the molecular dimensions as block length and diameters is relatively well understood. In so-called rod-coil block copolymers, the self-assembly behaviour is additionally influenced by aggregation/crystallization of the rigid-rod blocks. Conjugated rod-rod block copolymers can exhibit a spontaneous formation of nanosized meso- and nanostructures in thin films or layers.

However, such block copolymers reported until today consist of two or more hydrophilic (lipophilic) blocks which again limits their potential application in aqueous or bio-mimetic environments.^[i] Therefore, there is a great challenge to develop conjugated block copolymers containing both hydrophilic and hydrophobic conjugated blocks.

Here, we present novel amphiphilic, conjugated block copolymers, which form defined supramolecular nanostructures like vesicles as reported for rod-coil and hydrophobic rod-rod block copolymers. Moreover, the polarity of the medium used in self assembly process should allow some additional control over the nanostructure formation.^[ii]

Optical Properties & Behaviour:

UV/VIS



PL

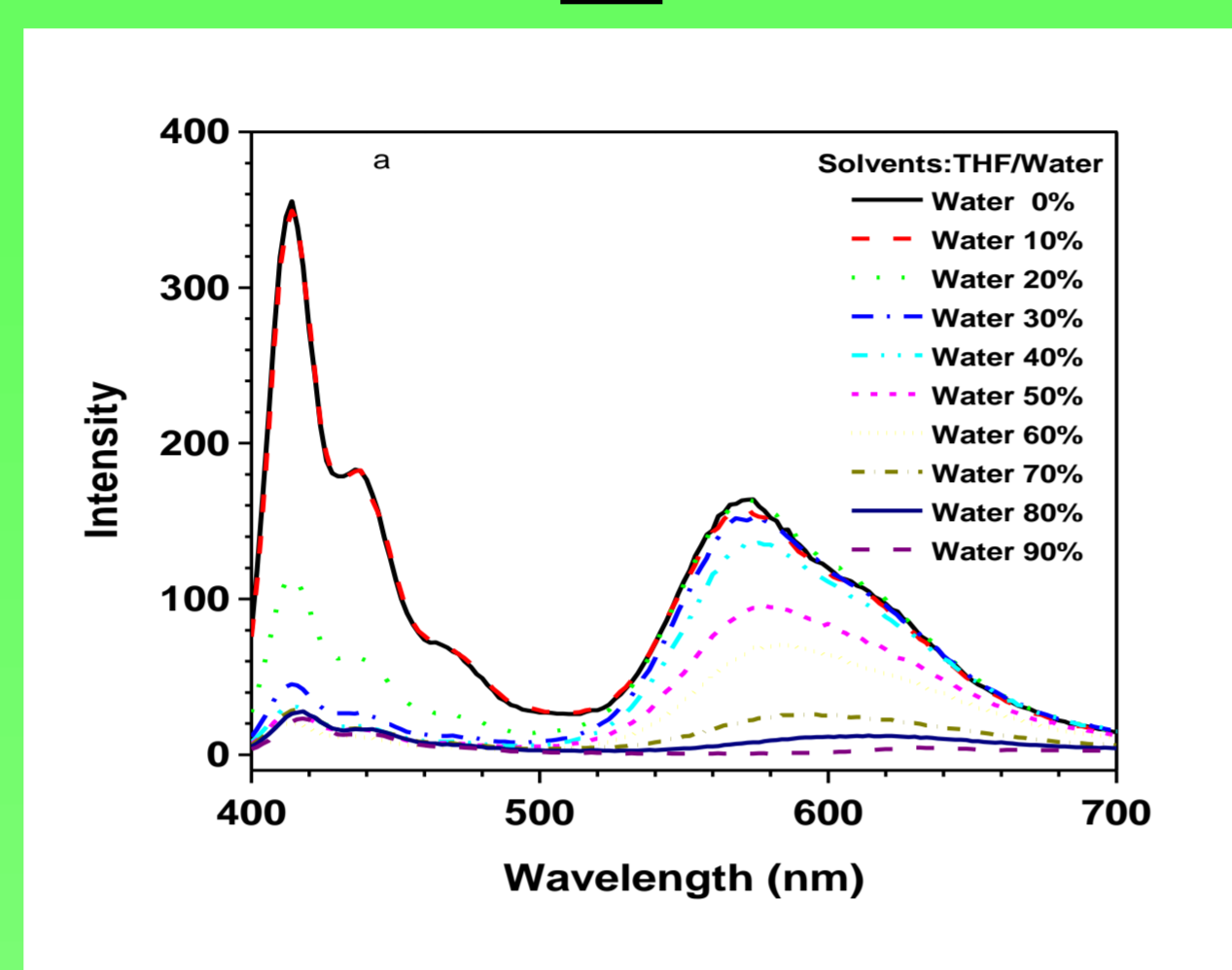


Fig. 1 and Fig. 2:

UV/Vis-absorption spectra (left side) and photoluminescence spectra (right side) of **P2** in THF/water mixtures

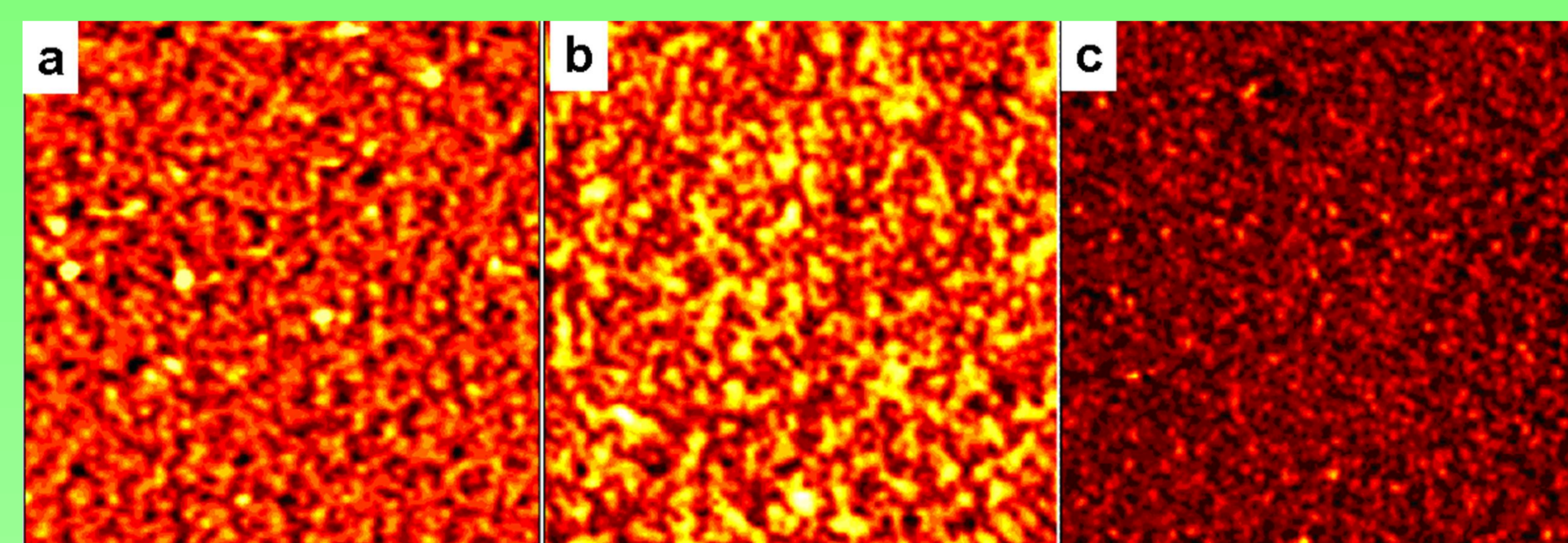


Fig. 3:

Contact-mode atomic force microscopy (AFM) images (5 x 5 mm) of drop cast thin films of **P2** on mica from different solvent mixtures (conc. 3.3×10^{-2} mg/ml): (a) THF/water (70:30 v/v), (b) THF/water (20:80 v/v), (c) THF/water (10:90 v/v), Z range 20 nm

AFM

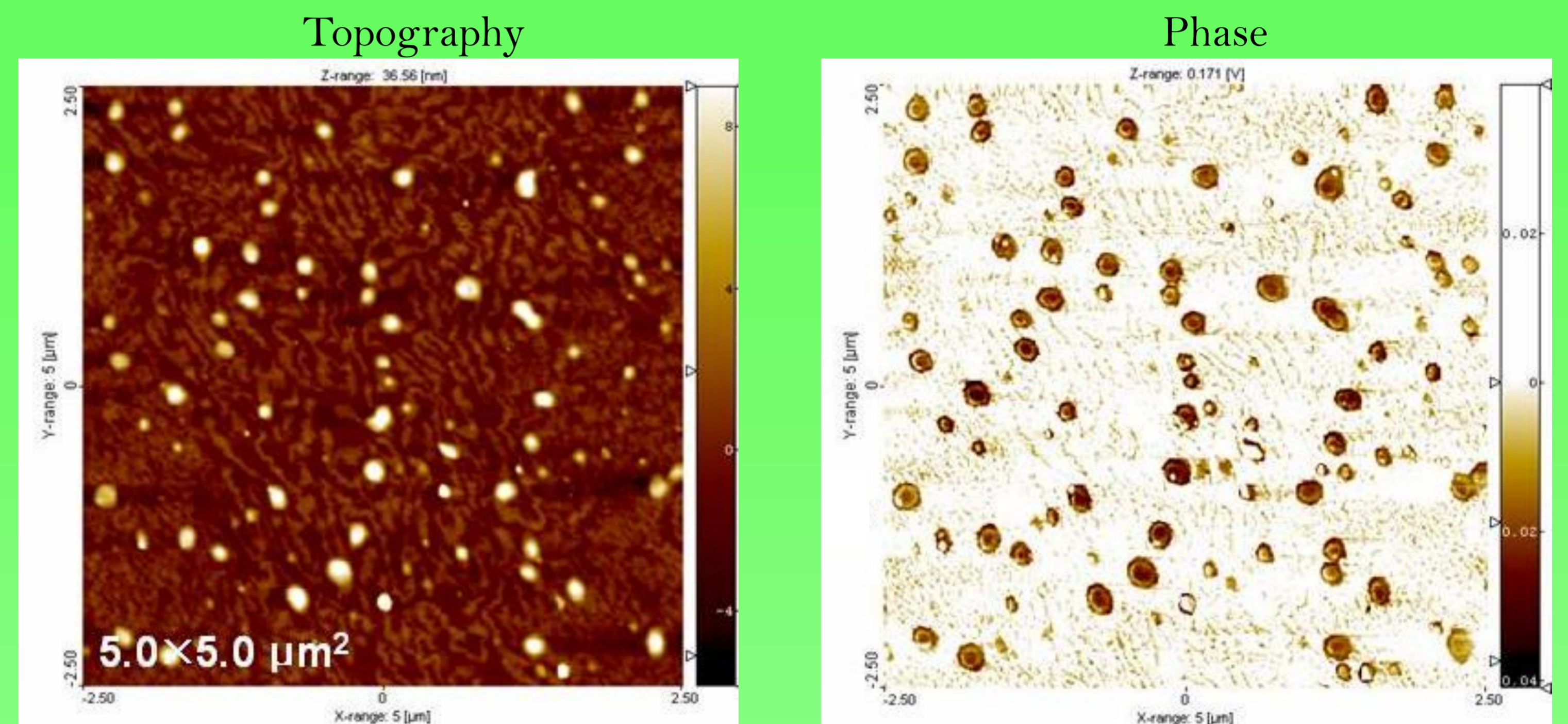
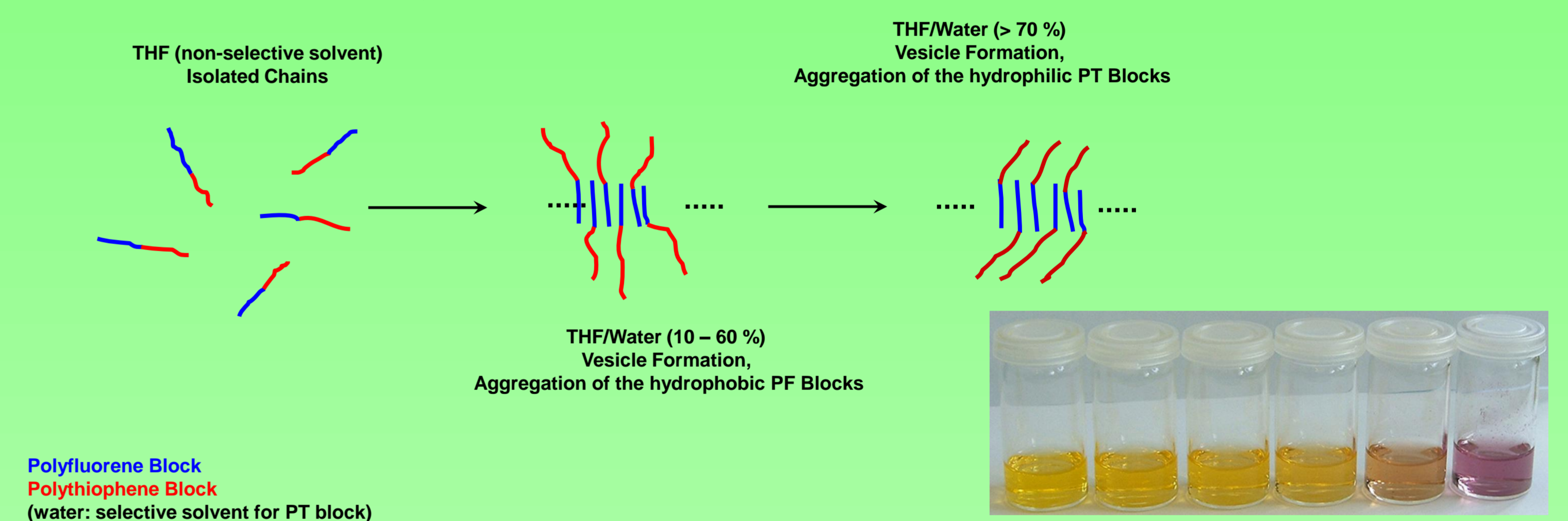
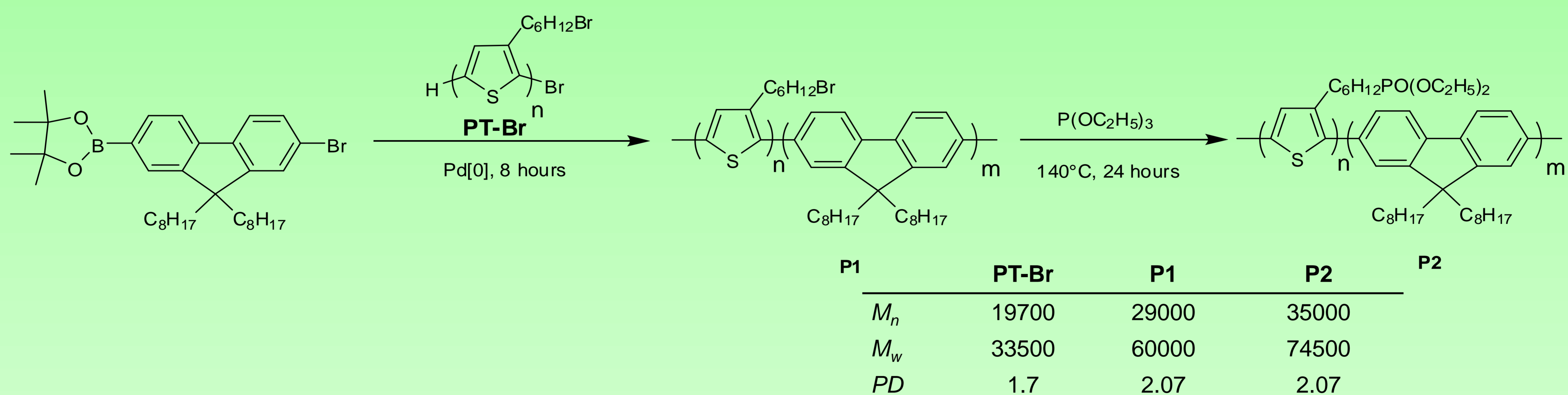


Fig. 4:

Contact-mode atomic force microscopy (AFM) images (5 x 5 mm) of LB monolayers of **P2** on silicon substrates by the group of Prof. R. Advincula, University of Houston.^[iii]



Synthesis:



Results:

- The polythiophene-related band of **P2** shows a solvatochromic shift effect from λ_{max} 450 nm to 540 nm with increasing water content. The distinct isosbestic point observed at ca. 485 nm indicates only two species, isolated chains and aggregation species
- The photoluminescence spectra of **P2** in THF/water mixtures show a two-step PL quenching process with increasing amount of water. The formation of aggregated PF2/6-blocks with isolated dissolved P3HT-blocks is observed.
- In THF/hexane mixtures the emission of the P3HT blocks is subsequently quenched without significant changes of the PF2/6-related emission. This indicates an aggregation process starting with an agglomeration of the P3HT-blocks under formation of vesicular particles
- The AFM images indicate that **P2** forms vesicles in the THF/water mixture with water contents > 30%. In the THF/hexane mixtures only at hexane contents > 80% particle formation is observed

[i] S. I. Stupp, *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 20; H.-A. Klok, S. Lemmandoux *Adv. Mater.*, **2001**, *13*, 1217; B. Gallot, *Prog. Polym. Sci.* **1996**, *21*, 1035 ; M. Lee, B.-K. Cho, W.-C. Zin, *Chem Rev.* **2001**, *101*, 1217; J. T. Chen, E. L. Thomas, C. K. Ober, G. P. Mao *Science* **1996**, *273*, 343. [ii] G. Tu, H. Li, M. Forster, R. Heiderhoff, L. J. Balk, R. Sigel, U. Scherf, *Small*, *3* (2007) 1001; [iii] U. Scherf, A. Gutacker, N. Koenen, *Acc. Chem. Res.*, *3* (2008) DOI: 10.1021/ar7002539; N. Koenen, U. Scherf, R. Advincula, *Macromolecules*, accepted; [iv] I. Zhai, R. D. McCullough, *Adv. Mater.*, *14* (2002) 901