

Supporting Information

Single-Step Shaping of Fluorescent Polymer Beads by Reverse Breath Figures Approach

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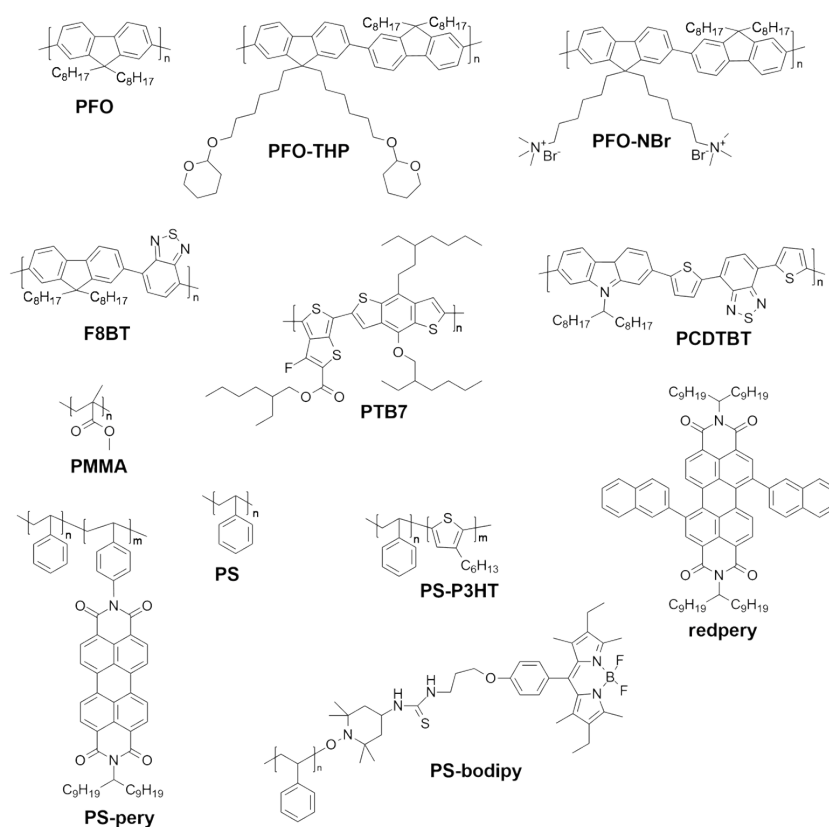
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Instruments and Methods

Optical measurements: PL spectra were recorded by liquid nitrogen cooled charge-coupled device combined with monochromator (Spex 270M), and excited using a monochromated xenon lamp.

Microscopy: Fluorescence microscopy images were obtained by using a Nikon Eclipse TE2000-U inverted confocal microscope. SEM micrographs were obtained by using a Scanning Electron Microscope SUPRA 40, after plasma sputtering of a thin layer of gold. AFM analyses were performed using a NT-MDT NTEGRA apparatus in tapping mode under ambient conditions.

Structure and properties of all materials tested



Scheme S1. Molecular structures of the materials tested.

Table S1. List of materials tested under modified RBF procedure and description of the results.

<i>Material</i>	<i>Origin</i>	M_w^a [kDa]	M_w/M_n^a	<i>Nanoparticle formation^b</i>	<i>Nanoparticle shape</i>
PFO	ADS	40-150	n.a.	✓	spheres and hemispheres
PFO-THP	ISMAC lab	72	2.8	✓	spheres and hemispheres
PFO-NBr	ISMAC lab	50	3.5	✗	-
F8BT	ADS	15-200	n.a.	✓	sphere clusters
PTB7	Aldrich	80-200	≤ 3.0	✓	spheres and hemispheres
PCDTBT	Aldrich		n.a.	✓	sphere clusters
PMMA	Polysciences	60	1.1	✓	holey discs
PS	Aldrich	230	1.6	✓	spheres and hemispheres
PS-bodipy	ISMAC lab	23	1.7	✓	hemispheres and discs
PS-pery	ISMAC lab	30	1.5	✓	spheres and discs
PS-P3HT	ISMAC lab	35	2.1	✓	spheres and hemispheres
redpery	ISMAC lab	1	1	✗	-
PS/redpery blend	Aldrich/ISMAC lab	230/1	1.6	✓	spheres and hemispheres

^a Measured by size-exclusion chromatography using PS as reference, for materials synthesized in our laboratory; as reported by the producer, for the purchased materials.

^b ✓ : Successful attempt; ✗ : unsuccessful attempt

Influence of humidity

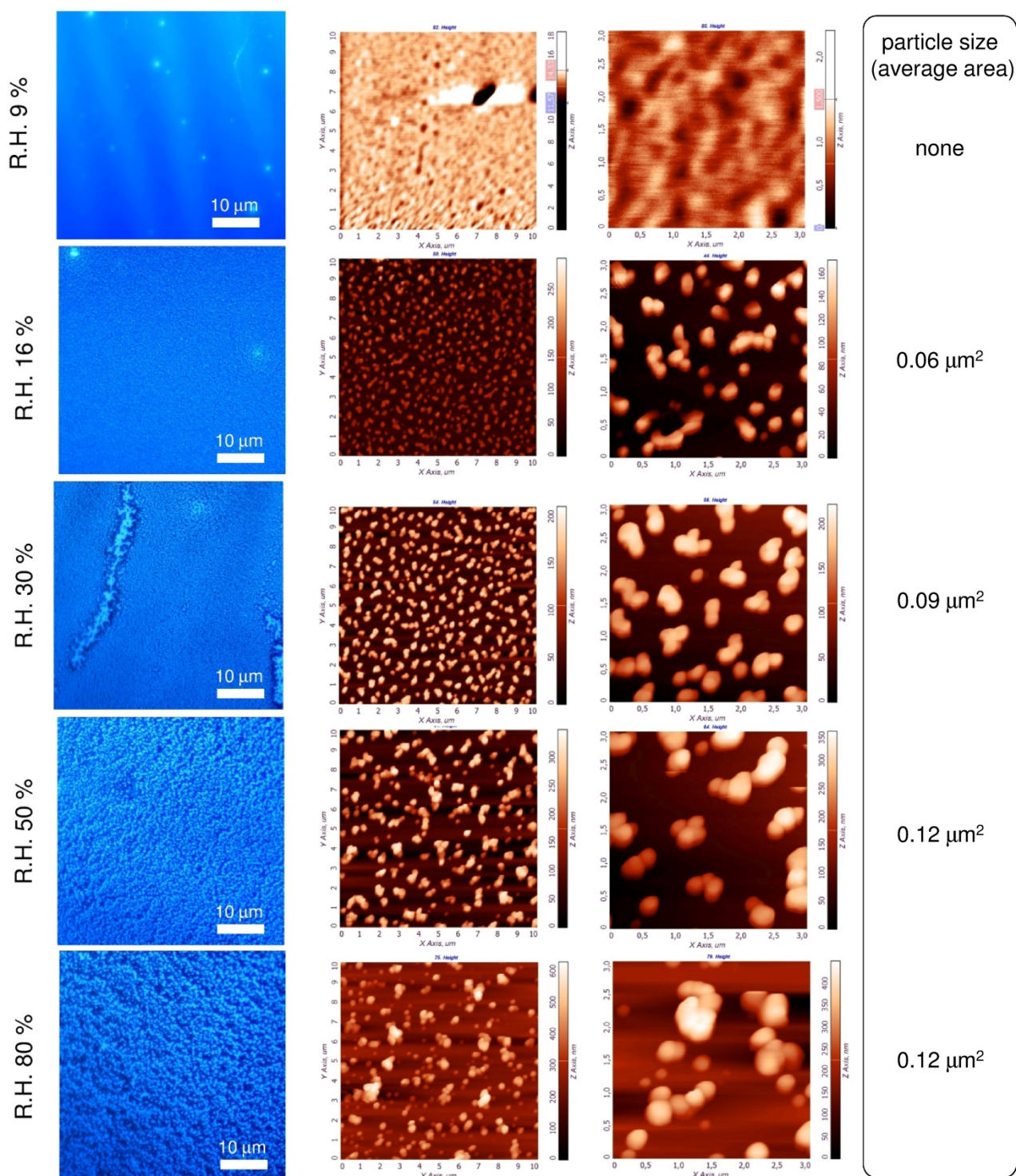


Figure S1. Fluorescence microscopy images (first column) and AFM tapping-mode images (second column $10 \times 10 \mu\text{m}$ scan; third column $3 \times 3 \mu\text{m}$ scan) of films prepared by spin-coating THF solutions ($2 \text{ mg}\cdot\text{mL}^{-1}$) of commercial PFO under nitrogen flow regulated at different R.H., from 9% (first row) to 80% (last row). In the last column the calculated average area particle is reported. Particles formation is observed from R.H. 16%. Calculated RMS roughness for the flat film obtained at R.H. 9% is 0.67 nm (from $10 \times 10 \mu\text{m}$ scan).

Microscopy comparison between RBF attempts using different materials and in different conditions

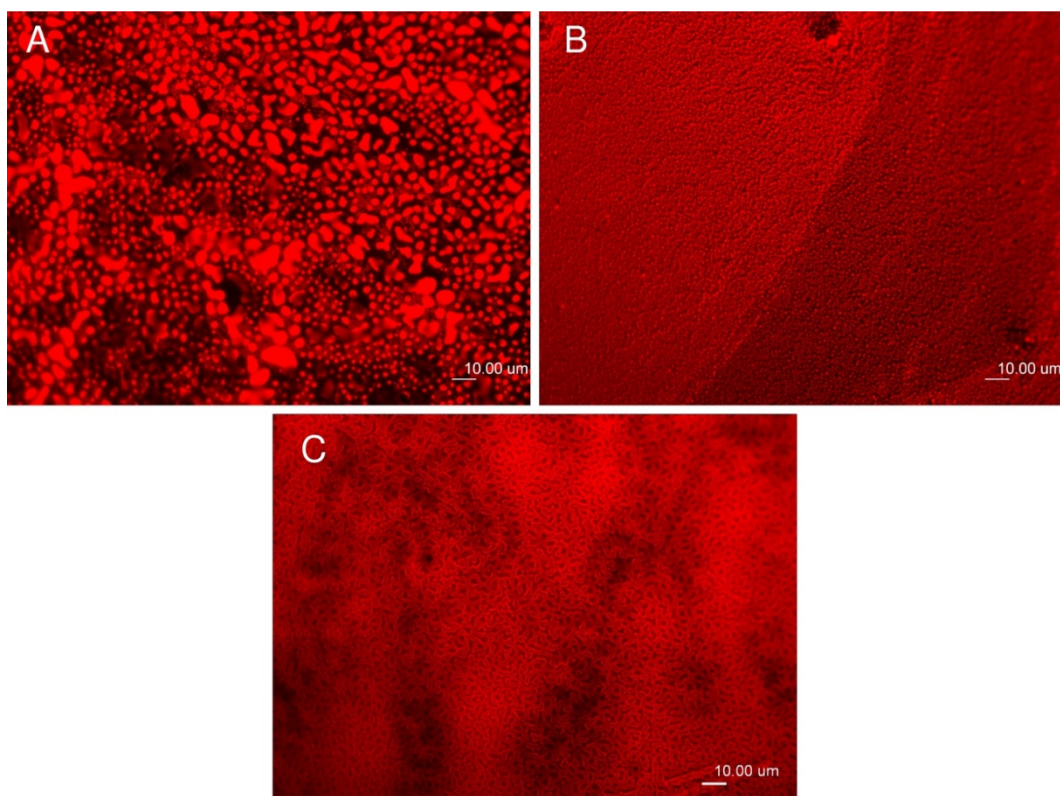


Figure S2. Fluorescence microscopy images of films prepared by spin-coating THF solutions (2 mg·mL⁻¹) of redpery (A) and of PS/redpery 20:1 (B) under humid nitrogen flow, and of PS/redpery 20:1 without humid nitrogen flow (C).

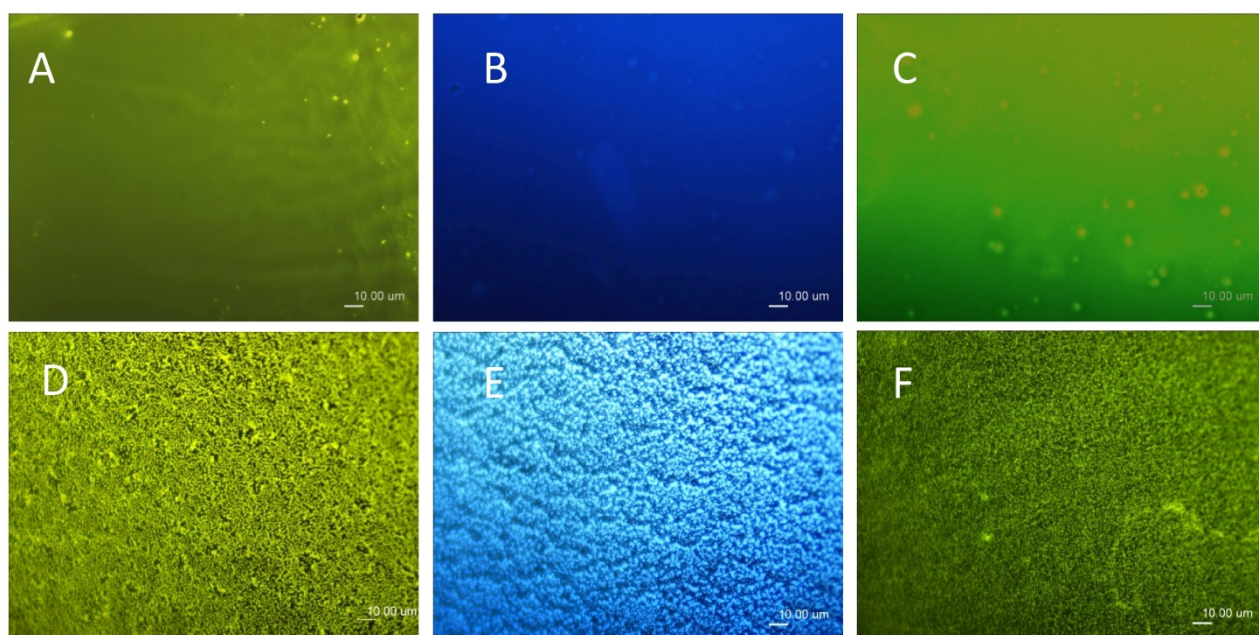


Figure S3. Fluorescence microscopy images of films prepared by spin-coating THF solutions (5 mg·mL⁻¹) of PF8BT (A, D), PFO (B, E) and PS-bodipy (C, F). Films shown in the first row (A-C) were prepared without humid nitrogen flow; films shown in the second row (D-F) were prepared under humid nitrogen flow.

PL analysis of single and multiple sequential depositions

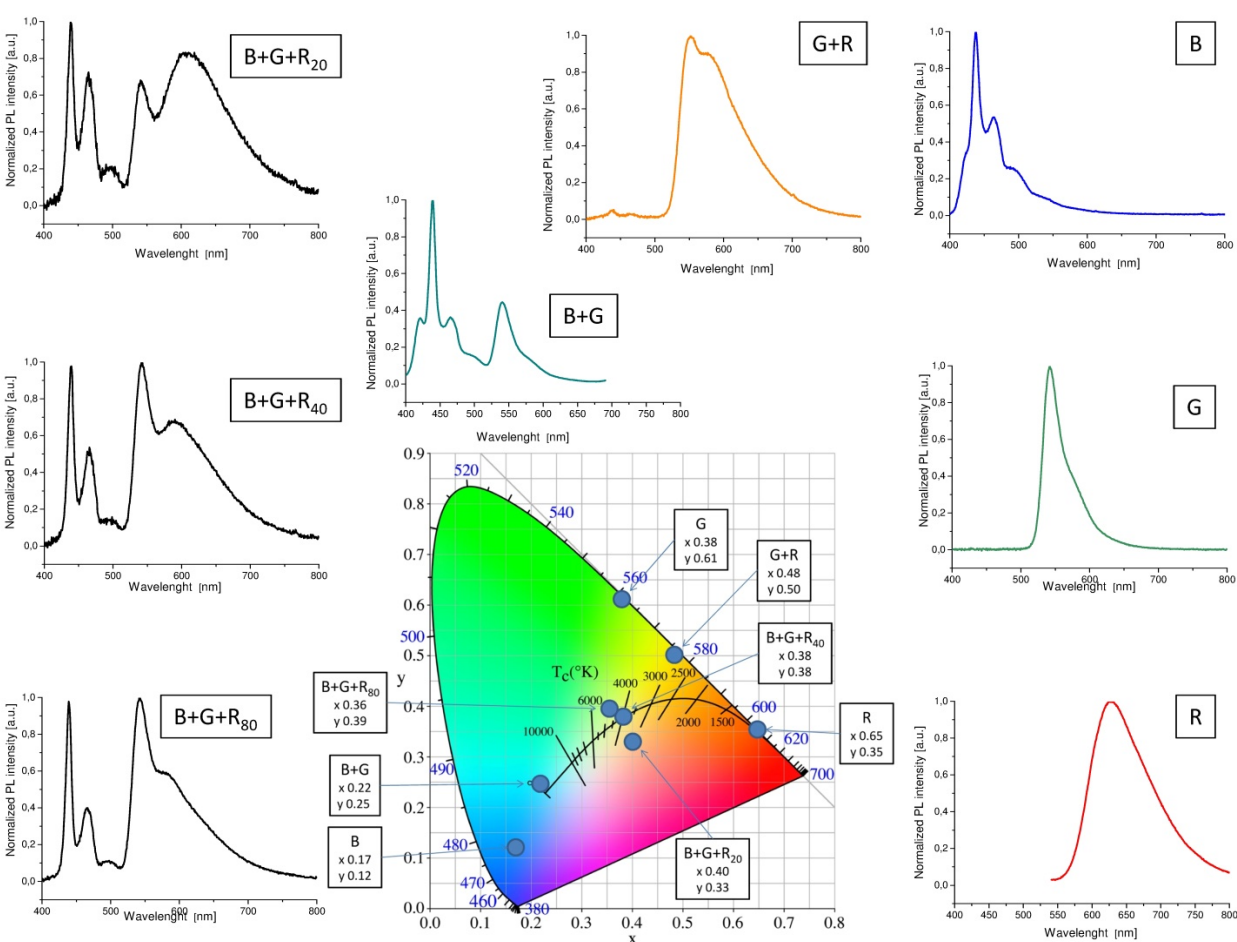


Figure S4. PL spectra of nanoparticle films prepared by both single and multiple sequential depositions of THF solutions, and corresponding CIE chromaticity coordinates plot. Clockwise from bottom left:

- B+G+R₈₀ = sequential depositions of PFO 5 mg·mL⁻¹ (B), PS-bodipy 10 mg·mL⁻¹ (G) and PS/redpery 80:1 (w/w) 1 mg·mL⁻¹ (R)
- B+G+R₄₀ = sequential depositions of PFO 5 mg·mL⁻¹ (B), PS-bodipy 10 mg·mL⁻¹ (G) and PS/redpery 40:1 (w/w) 1 mg·mL⁻¹ (R)
- B+G+R₂₀ = sequential depositions of PFO 5 mg·mL⁻¹ (B), PS-bodipy 10 mg·mL⁻¹ (G) and PS/redpery 20:1 (w/w) 1 mg·mL⁻¹ (R)
- B+G = sequential depositions of PFO 5 mg·mL⁻¹ (B) and PS-bodipy 10 mg·mL⁻¹ (G)
- G+R = sequential depositions of PS-bodipy 10 mg·mL⁻¹ (G) and PS/redpery 20:1 (w/w) 1 mg·mL⁻¹ (R)
- B = deposition of PFO 5 mg·mL⁻¹
- G = deposition of PS-bodipy 10 mg·mL⁻¹
- R = deposition of PS/redpery 20:1 (w/w) 2 mg·mL⁻¹

