

Supplementary Information

Polyfluorene Nano-rings and Nano-dots on a Surface: Evaporation Induced Polymer Self-Assemblies and Photoluminescence Properties of The Assemblies

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Experimental Section

General. All chemical materials and solvents were purchased from commercial suppliers and used without further purification unless otherwise noted. ^1H (399.00 MHz) and ^{13}C (100.00 MHz) NMR spectra were measured in a CDCl_3 solution at 25 °C on a JEOL EX-400 NMR spectrometer using tetramethylsilane as an internal standard. Weight-average molecular weight (M_w) and number-average molecular weight (M_n) were estimated by gel permeation chromatography (GPC) performed on a Shimadzu liquid chromatograph instrument equipped with a GPC column (Polymer Laboratories-Varian group, PLgel-mix type B) and a photodiode array detector (eluent: chloroform, 1.0 ml/min). Atomic force microscopy (AFM) was performed on a MultiMode scanning probe microscope (MM-SPM) and conducted with Nanoscope IV controller software V5.12 (Digital Instrument). Photoluminescence (PL) spectra were recorded on a JASCO FP-6600 spectrofluorometer equipped with a quartz-made set for measurements at low temperature.

Synthesis of polyfluorenes

A series of polyfluorenes (PFs) with various alkyl side-groups at the C-9 position were synthesized according to a synthetic approach described in the literature^[1] (Scheme 1). The 2,7-dibromo-9,9-dialkylfluorene monomers were prepared by double alkylation of 2,7-dibromofluorene (Aldrich) at the C-9 position in the presence of a strong base. The pure products were obtained by silica column chromatography purification followed by recrystallization in ethanol (Table 1). The PFs with various alkyl side-groups were synthesized by Yamamoto's coupling polymerization of 2,7-dibromo-9,9-dialkylfluorene monomers in the presence of $\text{Ni}(\text{COD})_2$ (Aldrich), which yielded polymers with high weight-average molecular weight up to 300,000. Polymeric products were obtained from filtration through a PTFE

membrane filter (0.45 μm pore) and precipitated twice in methanol from the crude products (Table 2). All monomers and polymers were confirmed by ^1H and ^{13}C NMR spectroscopy.

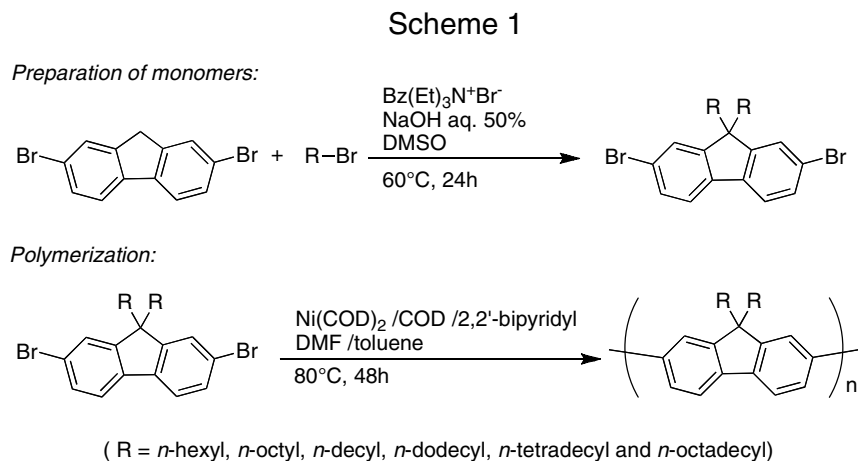


Table 1. Preparation of 2,7-dibromo-9,9-dialkylfluorene monomers.

Monomer	R group in 1	Isolated yield, %
F6	<i>n</i> -hexyl	90.0
F8	<i>n</i> -octyl	78.9
F10	<i>n</i> -decyl	77.2
F12	<i>n</i> -dodecyl	81.6
F14	<i>n</i> -tetradecyl	87.3
F18	<i>n</i> -octadecyl	87.0

Table 2. Characteristics of **PFs**.

Polymer	R group	Yield, %	$M_n (\times 10^4)^b$	$M_w (\times 10^4)^b$	PDI
(a) PF6	<i>n</i> -hexyl	nd ^a	2.57	6.90	2.68
(b) PF8	<i>n</i> -octyl	88.5	3.39	10.30	3.04
(c) PF10	<i>n</i> -decyl	88.0	8.89	23.72	2.67
(d) PF12	<i>n</i> -dodecyl	91.1	9.17	28.40	3.10
(e) PF14	<i>n</i> -tetradecyl	89.7	10.66	29.27	2.75
(f) PF18	<i>n</i> -octadecyl	87.1	4.54	11.70	2.58

^a Yield was not determined; ^b determined by GPC with polystyrene standards.

Results and Discussion

Supplementary results on the ring size:

The predominant rings formed were about 100-200 nm in diameter and about 1-3 nm in height, as determined by a statistical analysis of the 48 total ring-like assemblies in a 5 x 5 μm^2 area. It is known that the vertical resolution in AFM analysis is primarily determined by the resolution of the movement of the vertical scanner, which is < 0.1 nm, but the horizontal resolution strongly depends on the scan size and the tip shape (tip radius of curvature and the side-wall angle).^[2a] Therefore, the band width of the ring measured from the AFM images is relatively inaccurate compared with the height result. In Figure S2, we can see that the band width of the rings measured from an AFM image scanned in 2.5 μm is up to 30 nm, while it is reduced to ~20 nm from an image in 500 nm scan-size. Because the resolution on a 500-nm-scale is about 1 nm (500 nm/512 = 0.98 nm), which is much more accurate than the ~5 nm on a

2.5- μm -scale, the real band-width of the rings is probably about 20 nm after subtracting the positive error caused by tip-shape effects^[2b].

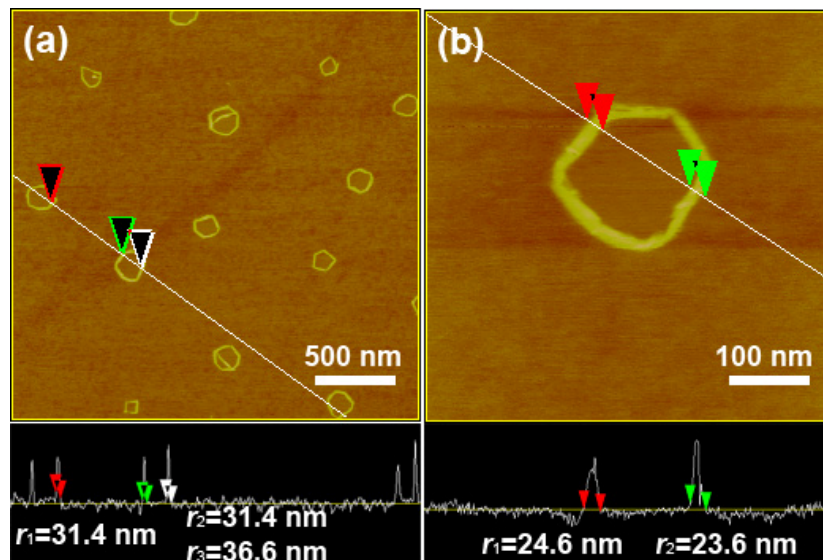


Figure S1. AFM images and the section analyses of the ring width of the **PF10** ring.

A simple, simulated model of a PF oligomer (by Chem3D, CambridgeSoft) suggests that the PF molecular chain in the plane is about 2.8 nm in width and 1.3 nm in thickness (Figure S2). The main-chain length to molecular weight is estimated to be about 187 nm/(10⁵ Da). The PF nano-rings average 150 nm in diameter and 2 nm in height with a band-width of 20 nm. The PL spectra suggest that the polymers exist in a planar conformation and ordered inter-chain packing like the ' β -phase' of **PF8**^[3] in the ring-like assemblies. We assume that the nano-rings were formed by several linear **PF10** molecules looped together around a water droplet nucleus. Their main-chains are probably in a semi-parallel alignment assisted by the main-chain π - π interaction and the alkyl side-chain packing.

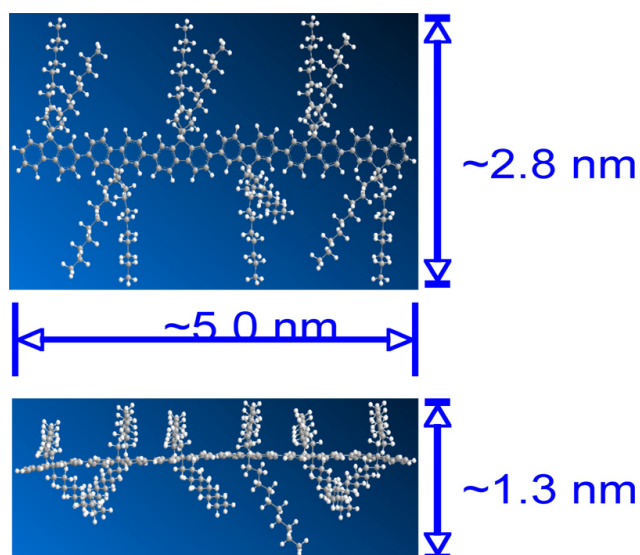


Figure S2. A six-unit oligomer model of PF10. The chemical conformation was optimized by energy minimization conducted with Chem3D software (Gamess/PM3 method).

A possible formation mechanism of PF nano-rings

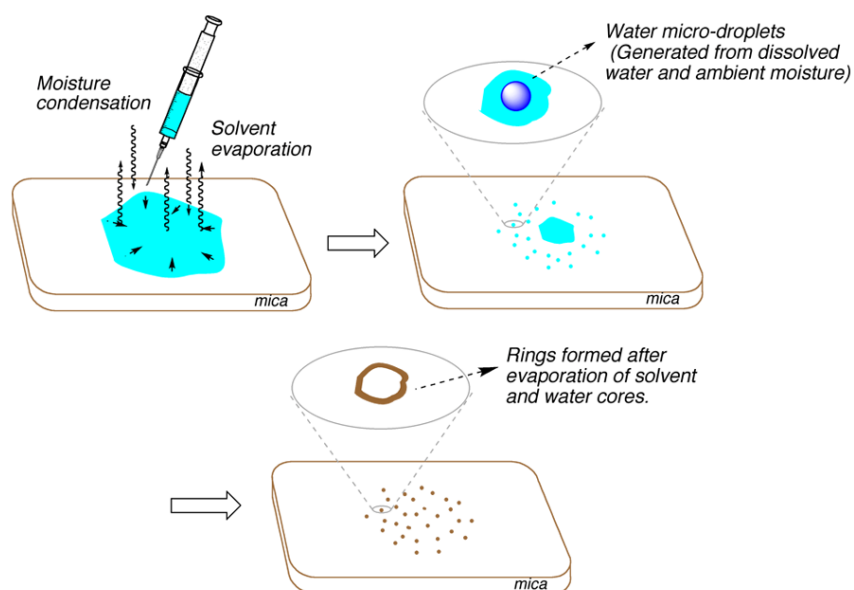


Figure S3. A proposed formation mechanism of polyfluorene nano-rings.

References

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