Supplementary Materials

Hierarchically Structured, Blue-Emitting Polymer Hybrids through Surface-Initiated Nitroxide-Mediated Polymerization and Water Templated Assembly

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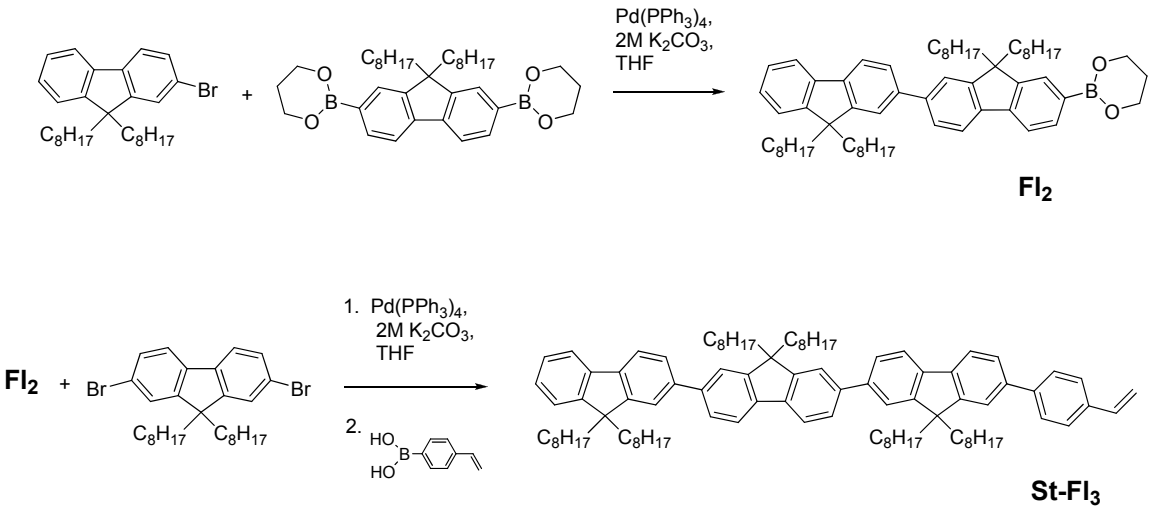
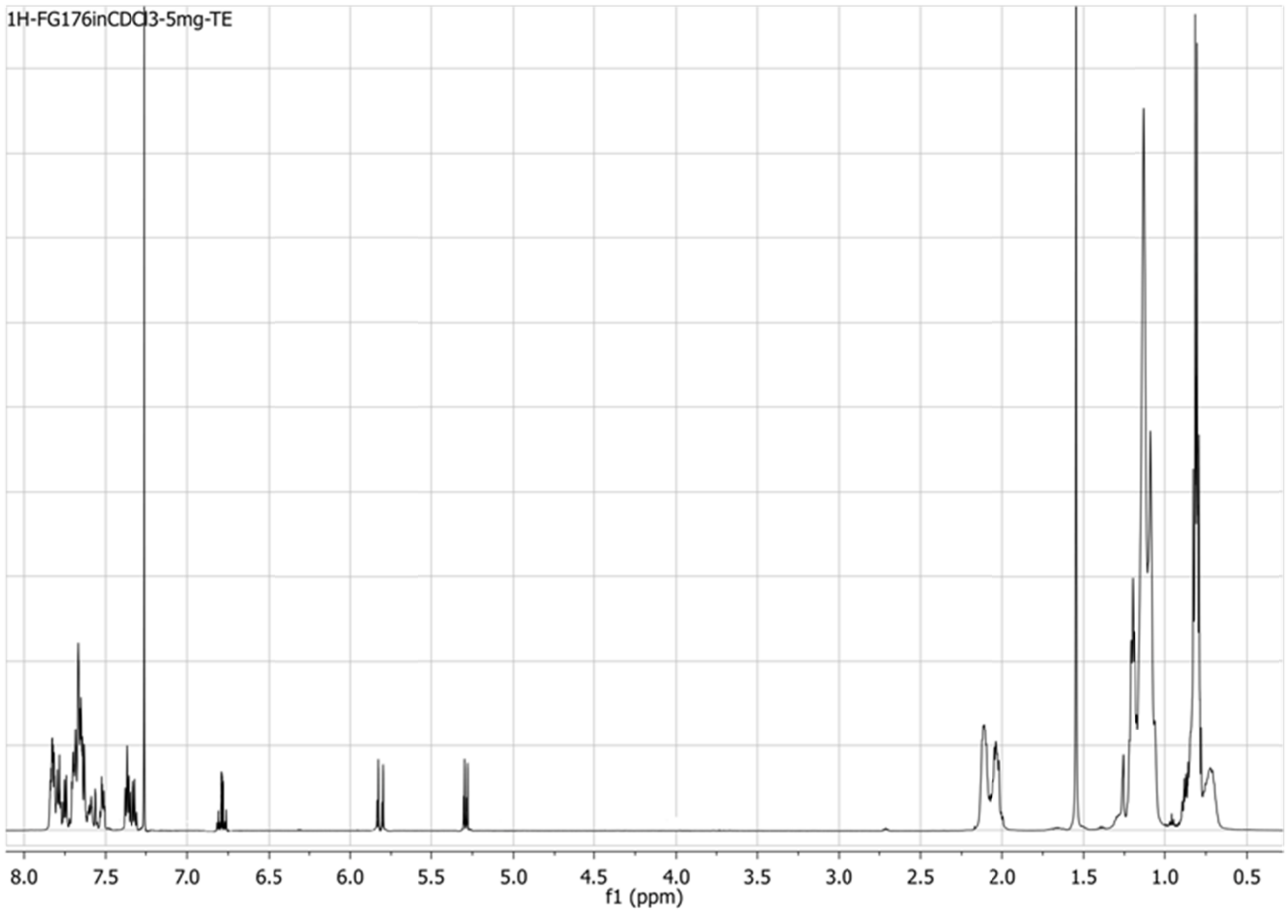


Scheme S1. Synthesis of 9,9-Dioctyl-2-(9,9-dioctyl-2-(9,9-dioctyl-2-(4-vinylphenyl)-9*H*-fluoren-7-yl)-9*H*-fluoren-7-yl)-9*H*-fluorene (St-Fl_3).



1H NMR in $CDCl_3$ of 9,9-Dioctyl-2-(9,9-dioctyl-2-(9,9-dioctyl-2-(4-vinylphenyl)-9*H*-fluoren-7-yl)-9*H*-fluoren-7-yl)-9*H*-fluorene (St-Fl_3).

TGA and DSC data

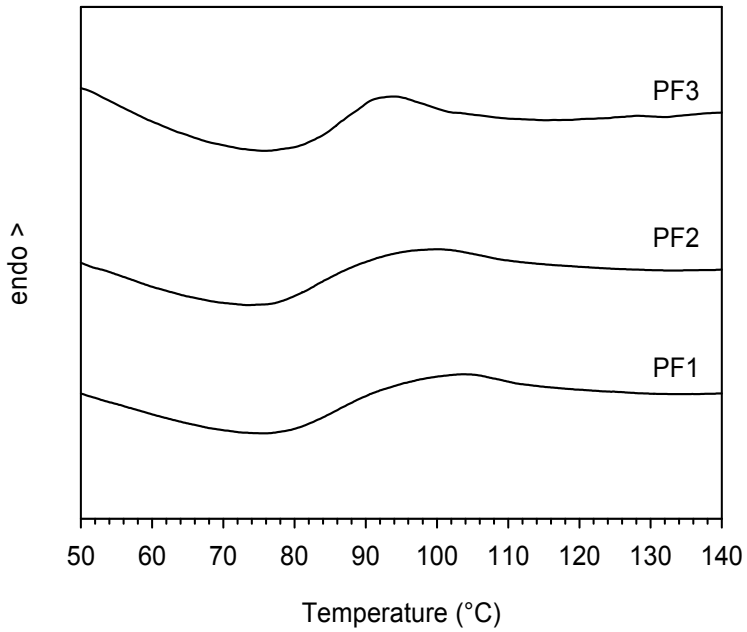


Figure S1. DSC second heating scan of the poly(St−*co*−St-Fl_3) hybrids: PF1, PF2, PF3.

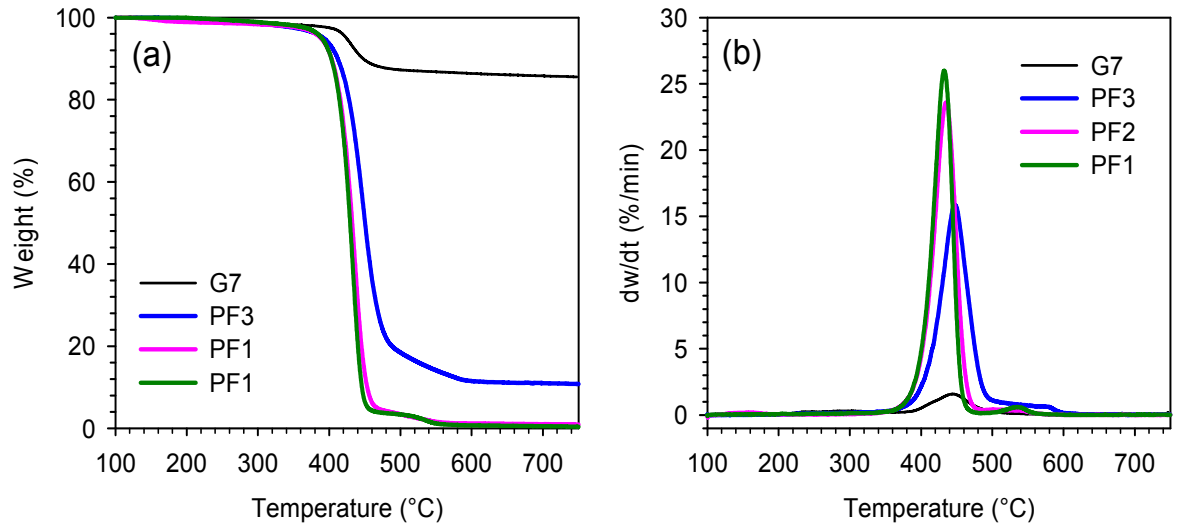


Figure S2. TGA (a) and DTG (b) curves under a nitrogen flow of the polymer hybrids PF1, PF2 and PF3 under investigation. As an aid to the discussion, the polymerization precursor G7 (black line) is reported and was published in ref 3.

Table S1. TGA and DSC data of PF1-3 polymer hybrids.

sample	T_{deg}[a] (°C)	Weight loss[b] (%)	R_{air}[c] (%)	T_g[d] (°C)
PF1	432	99.6	0.2	87
PF2	435	99.0	0.6	85
PF3	447	89.2	5.4	86

[*a*] T_{deg}, maximum decomposition temperature evaluated by TGA; [*b*] Total weight loss in the temperature range 100-750 °C under inert atmosphere by TGA; [*c*] R_{air}, residue at 750 °C under oxidative atmosphere by TGA; [*d*] T_g, glass transition temperature determined by DSC on second heating scan.

Table S2. TGA results.

sample	Weight loss[a] (%)	R_{air}[b] (%)
G7	17	82
St-Fl_3	68	0
St	100	0

[*a*] Total weight loss in the temperature range 100-750 °C under inert atmosphere by TGA; [b] R_{air}, residue at 750 °C under oxidative atmosphere by TGA.

Calculation of polymer hybrids composition

The amounts of G7, St and St-Fl_3 in the polymer hybrids, already reported in the Table 1 in the manuscript, were determined from TGA data, according to Smitha *et al*. [1]

Specifically, TGA data useful for evaluating the composition of the poly(St−*co*−St-Fl_3) hybrids (PF1−3) are reported in Table S2.

The G7 content was calculated according to eq. 1:

(eq. 1) $$G7 = \frac{R_{air}}{0.82} \quad (wt\%)$$

where R_{air} is the residue at 750 °C under oxidative atmosphere and 82% is TGA residue of G7 under oxidative conditions.

The St-Fl_3 content was calculated according to eq. 2:

(eq. 2) $$StFl_3 = \frac{[(100-W)-0.83\times G7]}{0.32} \quad (wt\%)$$

where W is the weight loss between 100 and 750 °C, 32% and 83% are the residues of TGA carried out under nitrogen flow of $StFl_3$ and G7, respectively.

The St content was calculated according to eq. 3:

(eq. 3) $$St = 100 - (G7 + StFl_3) \quad (wt\%)$$

where G7 and $StFl_3$ are the amounts determined by eq. (1) and (2), respectively.

Optical Characterization

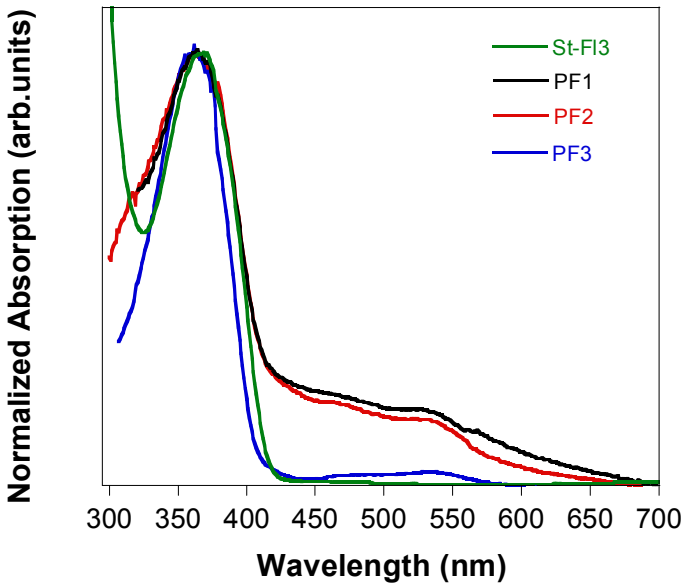


Figure S3. Normalized UV-Vis spectra of PF1-3 polymer hybrids and St-Fl_3 films.

Table S3. PL quantum yields of PF1-3 polymer hybrids in toluene solution, measured respect to quinine sulfate.

sample	PL-QY
PF1	0.72
PF2	0.80
PF3	0.70

Images of PF3 films and solution.

The following figures show full pictures of patterned films of PF3 taken with fluorescence microscope.

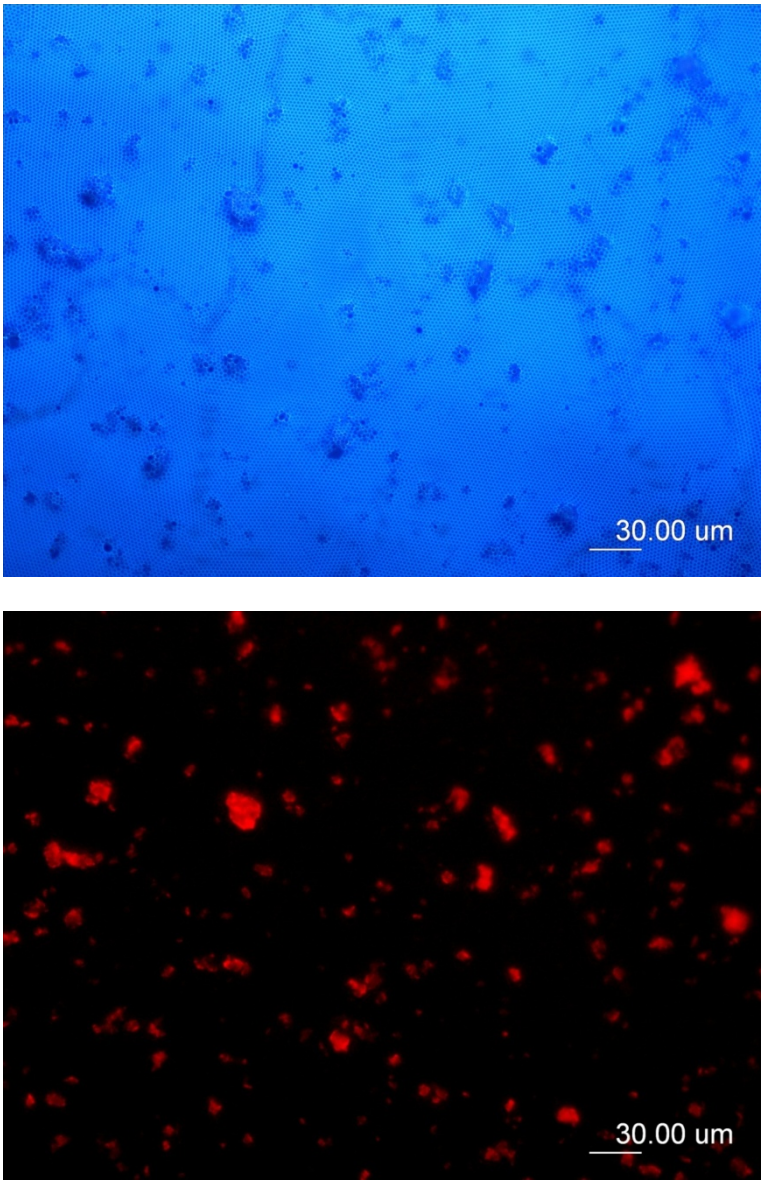


Figure S4. Fluorescence view taken with UV excitation, showing long-range order of the honeycomb film (top). Same view taken with green excitation, showing the random distribution of R6G filled silicates in the film (bottom). Since the polymer is not excited by this excitation light, the honeycomb film is not visible.

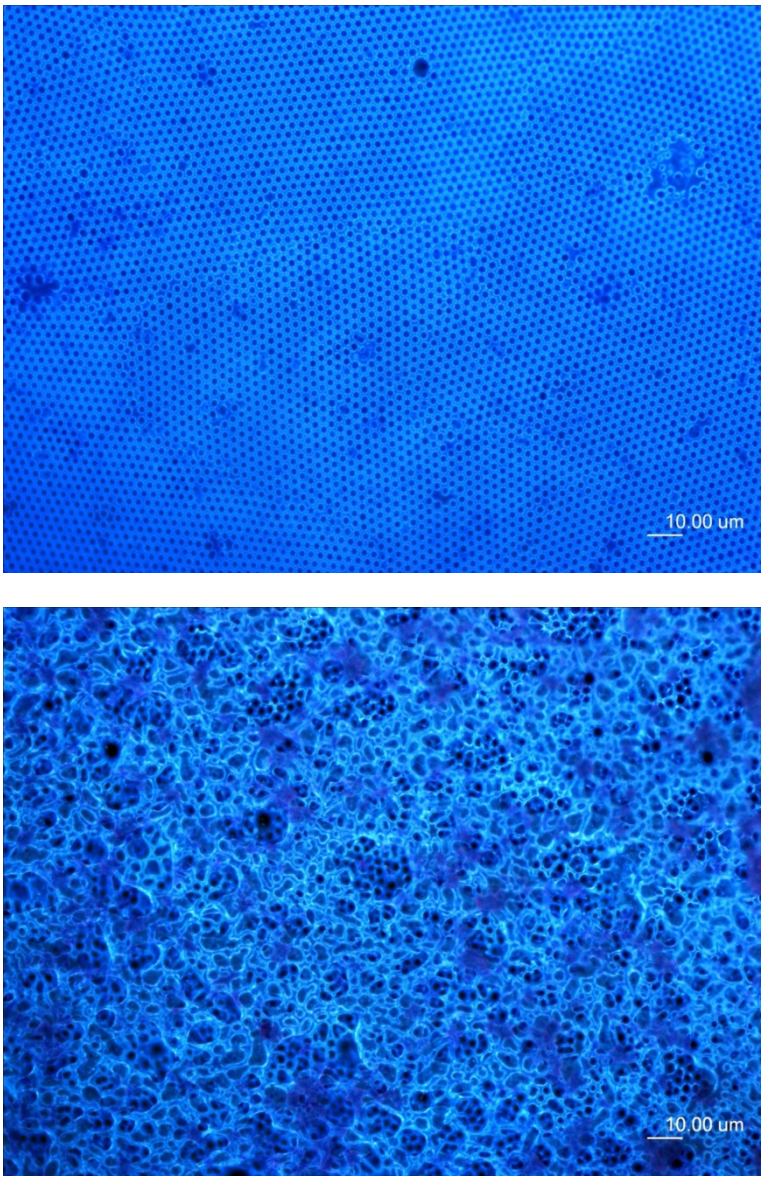


Figure S5. Fluorescence view taken with UV excitation, at a biggest magnification as compared to the previous. Picture taken by focusing on the top surface of the honeycomb film (top). Picture of the same sample taken by focusing on the bottom, from the glass cover slip used as substrate, showing through porosity of the film (bottom).

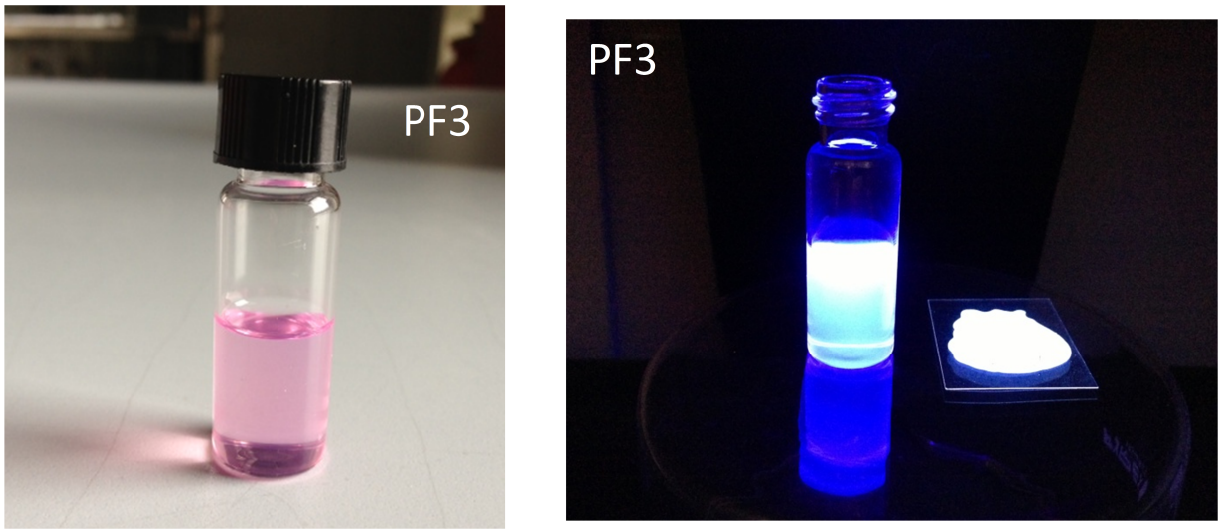


Figure S6. Photographs of a diluted toluene solution of PF3 taken under ambient light (left) and of PF3 solution and film taken under UV lamp at 354 nm (right).

References

[1] V. S. Smitha, K. A. Manjumol, S. Ghosh, M. Brahmakumar, C. Pavithran, P. Perumal, K. G. Warrier, *J. Am. Ceram. Soc.*, **2011**, *94*, 1731-1753.