Preparation of *n*-Type Semiconducting Polymer Nanoarrays by Covalent Synthesis Followed By Crystallization

Fouzia Begum [a], John Ferguson[a], Kelly McKenna [a], Louis E. McNamara[b], Nathan Hammer[b*], and Hemali Rathnayake[a*]

[a] Department of Chemistry, Western Kentucky University, Bowling Green, KY 42101; [b] Department of Chemistry & Biochemistry, University of Mississippi, MS 38677;

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Experimental

Materials. 3,4,9,10-tetracarboxyanhydrideperylene, anhydrous methanol (99% purity), and Ammonium hydroxide (28%) were purchased from Aldrich chemicals. 3-aminopropyltriethoxysilane was purchased from Alfar Aesar and used as received. Unless otherwise specified, all chemicals were used as received.

Characterization. Proton NMR spectra were recorded on a 500 MHz Jeol using $CDCl_3$ as a solvent. FTIR spectra were measured using a Perkin-Elmer Spectrum One FT-IR spectrometer equipped with a universal ATR sampling accessory. Mass spectra were acquired by the University of Kentucky Mass Spectrometry Facility. Matrix-assisted laser desorption ionization mass (MALDI-TOFMS) spectra were obtained on a Bruker Daltonics (Billerica, MA) Ultraflextreme time-of-flight mass spectrometer with SmartBeam II Nd:YAG/355 nm laser operating at 200 Hz and laser focus set to "small" focus setting. Laser attenuation was optimized to obtain the best signal-to-noise (S/N) ratio, keeping maximum resolution. The sandwich method of sample preparation was employed with the matrix of ∝-cyano-4-hydroxycinnamic acid. The photophysical properties in solution were performed on fluorescence spectrometer (Perkin Elmer LS 55) and UV-visible spectrometer (Perkin Elmer, Lambda 35). Scanning electron microscopy (SEM) observations were performed on a 100CX JEOL at 80 keV.

Thin film emission spectra and excited state lifetimes were acquired using a Nikon Eclipse TE2000-U

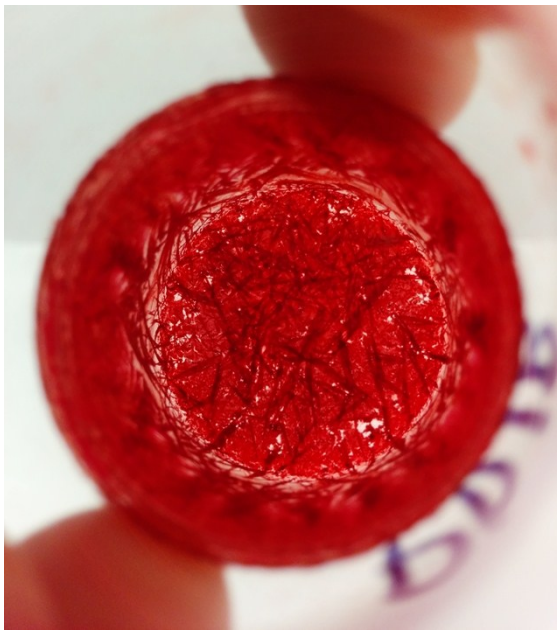
inverted microscope with a 1.4 numerical aperture objective and a 485 nm ps pulsed diode laser with EMCCD camera detection (Princeton Instruments ProEM 1024). Solid state (concentrated thin film) absorption spectra were acquired using a Agilent Technologies Cary Series UV-Vis-NIR Spectrophotometer.

Typical Procedure for the preparation of poly-PDIB-SSQ nanoarrays: 50 mg (0.063 mmol) Freshly prepared perylenediimide-bridged silane (50.0 mg, 0.063 mmol) was dissolved in 5.0 mL of chloroform and then sonicated for one minute. The solution was filtered through a 0.45 micron syringe filter into a 20 mL vial. In a separate vial, 4.0 mL methanol and 1.0 mL ammonium hydroxide were mixed and were added gently to the first vial with no disturbance to the silane solution in the vial. Unless the bottom layer was disturbed in which case the top layer would take on an opaque red color, the methanol ammonium hydroxide solution formed a clear top layer (see Figure S1(a)) and the perylenediimide bridged silane in chloroform comprising a translucent red lower layer. The interface between these two layers was opaque and red, growing overtime until no clear distinction could be made between the layers. After 48 hours, a dark red homogenous suspension was obtained. At this stage solution was allowed to evaporate slowly to yield long red color needles in the lower portion of the vial as shown in Figure S1 (b). FTIR stretching (cm^{-1}): 2993-2885 (C-H stretching of alkyl chains), 1691 (diimide carbonyl stretching), 1594-1647 (aromatic C-C stretching), 1440 (N-C stretching from perylenediimide), 1379-1250 (Si-C stretching), 1098-1016 (Si-O-). MS (MALDI-TOF, negative): *m/z* = 2274, 2393, 2973, and 3120 [M^-]. Elemental analysis (%): Experimental- C 63.56, H 4.14, N 4.70, Si 9.31; Calculated (assuming product was fully hydrolysed)- C 62.48, H 3.50, N 4.86, Si 9.74.

Post purification of polymer nanoarrays: The suspension obtained after 48 hours of reaction time was centrifuged and washed with methanol to yield a red solid. The wet solid was dissolved in minimum volume of chloroform in a vial and equal volume of methanol was slowly added to form two

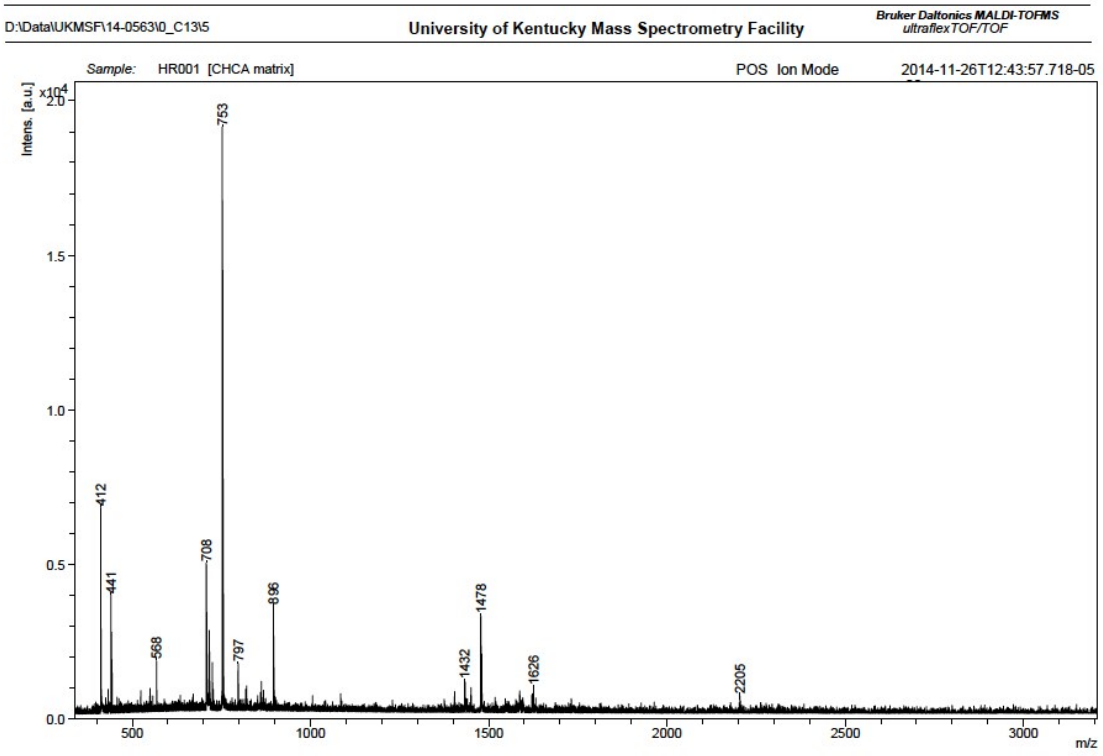
layers. The solution was tightly capped and kept with no disturbance. After 48 hours, the solution was allowed to evaporate slowly to yield crystals.

(a) Just after adding methanol/NH_4OH solution a



(b) Needles like long crystals after slow evaporation of the solution

Figure S1: (a) optical photograph of a reaction vial just after adding methanol; (b). Optical photograph of the reaction vial after the slow evaporation of the solution.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ultraflexTOF/TOF
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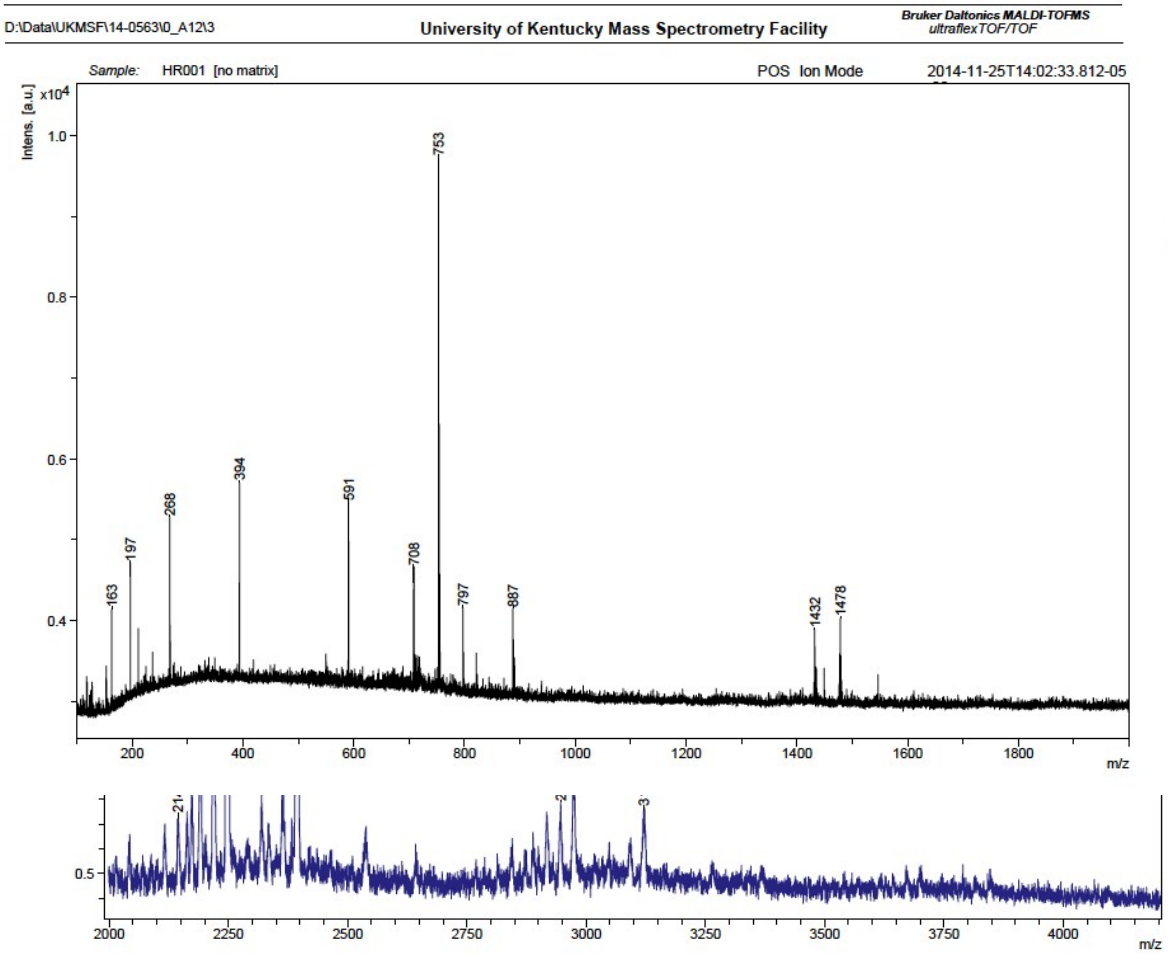
1478
1626
2205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University of Kentucky Mass Spectrometry Facility
Bruker Daltonics MALDI-TOFMS
ultraflexTOF/TOF
Sample: HR001 [no matrix]
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m/z
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197
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1478

Figure S2: MOLDI-TOF-MS spectral traces of poly-PDIB-SSQ nanoarrays

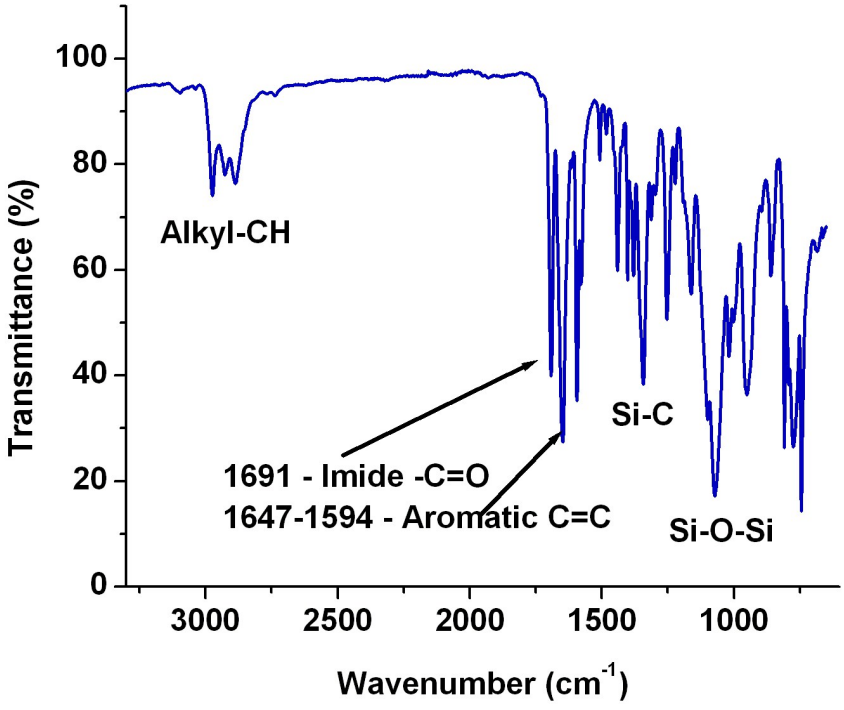

Figure S3: FTIR spectrum of poly-PDIB-SSQ nanoarrays

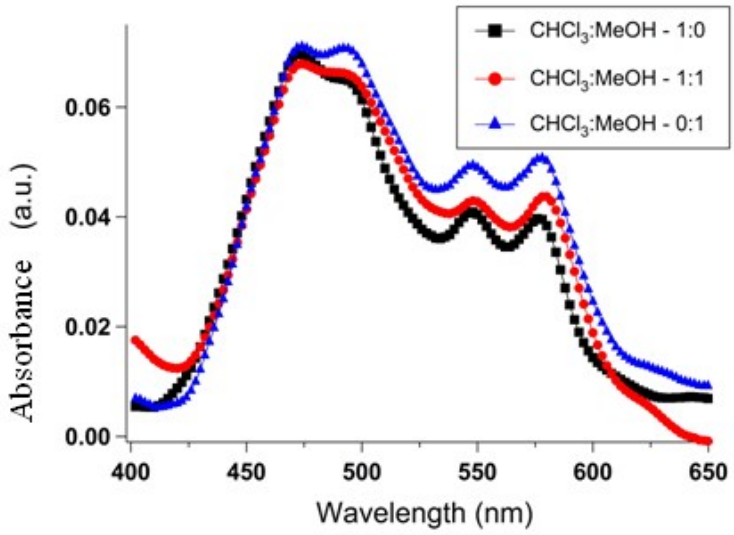

Figure S4: Solid state (concentrated thin film) absorption spectra of poly-PDI-SSQ nanoarrays from 1:0, 1:1, and 0:1 $CHCl_3$:MeOH solutions.