Supporting Information

for

Semiconducting Polymer-Dipeptide Nanostructures by Ultrasonically-Assisted Self-Assembling

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Experimental

General: P3HT and diphenylalanine and other regular chemicals were acquired from Sigma-Aldrich Co. and used without further purification. Emissive polymers poly(9,9-di-n-octylfluorenyl-2,7-diy) – PFO and poly[(9,9-dioctylfluorenyl-2,7-diy)-co-alt-(N,N'-diphenyl-N,N'di(p-butyl-oxy-phenyl)-1,4-diaminobenzene)] – PFOG were purchased from American Dye Source Inc. and poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] – PCDTBT from Ossila Limited.

An ultrasonic processor VCX600 model (Sonics & Materials Inc., Newtown, USA) adapted with a 3mm diameter tapered microtip operating at 20KHz was used for ultrasound-assisted synthesis.

AFM and optical microscopy images were taken using a Nanosurf EasyScan 2 (Nanosurf AG, Liestal Switzerland) and Olympus B51x (Olympus Corp., USA), respectively. IR spectra and maps were performed with a Nicolet model iN10 infrared microscope using a MCT detector cooled by liquid nitrogen. The XRD patterns were recorded on a PanAnalytical X’pert PRO Multi-Purpose Diffractometer, using Cu-Kα radiation (λ = 0.15418 nm), operating at 45 kV and 40 mA and equipped with a Parallel Plate Collimator detector. The measurements were carried out at 2θ angles ranging from 2.00 to 30.00 with a scan step size of 0.0500 using the grazing incidence diffraction geometry, where the incidence angle was ω = 1.50. TGA analysis were taken from a thermogravimetric analyzer model TGA-50/51 (Shimadzu Scientific Instruments, Columbia, USA) Circular dichroism spectra and cyclic voltammetry analysis were performed in a CD spectrometer model J720 (Jasco Analytical Instruments, Easton, USA) and in a potentiostat/galvanostat PGSTAT302N model (Metrohm Autolab, Utrecht, The Netherlands), respectively. SEM images were taken from a FEI Inspect F50 – High Resolution SEM (FEI Co., Hillsboro, USA) at LNNano - Brazilian Nanotechnology National Laboratory facilities.

Ultrasound intensity estimation: The ultrasound intensity delivered to the sample was varied by changing the amplitude at fixed frequency of 20 KHz and the ultrasound intensity was calculated as follow:

1) The amplitude was set in 10%, 20%, 33% and 40%.
2) For each amplitude, with the probe in air the amount of power in watts displayed in equipment’s monitor was recorded.

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3) Without changing the amplitude setting, the probe was immersed into the sample (1 cm) and again the amount of watts displayed on the power monitor was recorded.

4) The difference in power readings between step 2 and 3, is the amount of power being delivered to the sample in watts. The ultrasound intensity was estimated dividing the delivered power by area of the probe tip (3 mm tip = 0.0707 cm²). Table S1 below shows the ultrasound power delivered to the samples of FF:P3HT.

<table>
<thead>
<tr>
<th>Amplitude (%)</th>
<th>P_{delivered} [W]</th>
<th>I_{ultrasound} [W/cm²]</th>
<th>Delivered energy [J]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2</td>
<td>28.3</td>
<td>1800</td>
</tr>
<tr>
<td>20</td>
<td>4</td>
<td>56.6</td>
<td>3600</td>
</tr>
<tr>
<td>33</td>
<td>6</td>
<td>84.7</td>
<td>5400</td>
</tr>
<tr>
<td>40</td>
<td>7</td>
<td>99.0</td>
<td>6300</td>
</tr>
</tbody>
</table>

**Synthesis**: The hybrid FF:semiconducting polymer were prepared as briefly described in the paper. Herein, we provide more experimental details about the synthetic protocol.

**FF:P3HT**: In a 3 mL eppendorf tube, 5mg of diphenylalanine (L-Phe···L-Phe) were dissolved in 50 µL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFP). To the peptide solution, 850 µL of rr-P3HT solution in DCB (0.5 mg/mL) and 100 µL of DI water were consecutively added. The ultrasound microtip was immersed 1 cm into the solution and ultrasound intensity set by changing the amplitude (10, 20, 33 or 40%) as described above. The process of self-organization initiated spontaneously by the ultrasound energy giving rise to FF:P3HT hybrid material as a light-violet precipitated. The temperature was kept at 0-4 °C with an ice-water bath during all the process. After ceased the ultrasonic energy (15 min.) the material was allowed to stand for 8h. The crude product was washed and harvested with at least 3 centrifugation-redispersion cycles (2265 g) using DCB as solvent. Then, the resulting fibrous solid was finally dried in vacuum oven at 60 °C for 24h.

For the preparation of FF:PFO, FF:PCBTBT and FF:PFOG, exactly the same procedure was used just replacing the P3HT by the correspondent conjugated polymer. FF:PFO and FF:PFOG were isolated as fibrous light yellow solids presenting strong blue and green fluorescence, respectively.

**Solvent effect**

Preliminary experiments indicate the polymer solvent has effect on the morphology of the hybrid material obtained by ultrasound-assisted self-assembling. As shown in figure S1 a rich morphology can be produced range from nanosheets, nanotubes and a mixture of vesicles and nanotubes depending the selected solvent.
Cyclic Voltammetry data

Table S1 below shows the energy levels calculated by CV data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{onset}}^{\text{red}}$ [V]</th>
<th>$E_{\text{onset}}^{\text{oxi}}$ [V]</th>
<th>LUMO [eV]</th>
<th>HOMO [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FF</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P3HT</td>
<td>-1.77</td>
<td>0.18</td>
<td>3.13</td>
<td>5.08</td>
</tr>
<tr>
<td>FF:P3HT</td>
<td>-1.89</td>
<td>0.10</td>
<td>3.01</td>
<td>5.00</td>
</tr>
</tbody>
</table>

* In DCM (1 mM) with TBAPF6 as supporting electrolyte and scan rate 100 mV s$^{-1}$ in a three electrode cell. A carbon vitreous disk electrode and Pt disk were used as working and counter electrodes, respectively. $E_{\text{HOMO}} = - (E_{\text{onset}}^{\text{oxi}} \text{ vs } \text{Fc/Fc}^+ + 5.1 \text{ (eV)})$ $E_{\text{LUMO}} = - (E_{\text{onset}}^{\text{red}} \text{ vs } \text{Fc/Fc}^+ + 5.1 \text{ (eV)})$.

FT-IR mapping

The distribution of P3HT polymer over the FF nanostructures was evaluated by FTIR-mapping by setting individual frequencies of P3HT polymer. The figure S2 shows a typical map obtained for FF:P3HT self-assembled at 28.3 W/cm$^2$.

UV-Vis absorption and AFM

UV-Vis absorption spectra in solution and film for FF:P3HT show distinct quantum-confinement indicating the ultrasound-assisted self-assembly nanostructure can be interconverted from quantum-dots (vesicles) to nanobelts/nanowires upon solubilization in a particular mixture of solvents (Fig. S3).
The morphology of the FF:P3HT film is also dependent on the mixture of solvents and the concentration as evidenced by AFM microscopy (Fig. S4). For instance, if isopropanol is used in combination with ethanolamine the film consists only of nanobelts/nanowires. On the other hand, when 1-butanol is used vesicle-like are produced. If none ethanolamine is added such nanostructure interconversion is avoided.

**Figure S4.** AFM images of FF:P3HT films deposited on silicon substrates from different mixture of solvents.

**FET fabrication**

For P3HT and FF:P3HT-based transistor fabrication a commercial testing OFET structure was used (Fraunhofer IPMS, Dresden, Germany) in clean room, see Fig. S5. Prior to use, the silicon chips were cleaned with acetone and submitted to O₂ plasma treatment.
**P3HT FET**: For pure P3HT devices a 1 wt% solution of P3HT (Ossila Ltd.) in dichlorobenzene was deposited by spin-coating (15s@1500 rpm then 45s@300 rpm) and then annealed in oven at 120°C for 1h.

**FF:P3HT FET**: FF:P3HT material prepared as described above at 28.W ultrasound energy was dispersed in 1-butanol (1.88 g/mL). 50 µL of the dispersion was deposited by drop-casting on bottom-gate/bottom-contact device structure having n++-Si as gate, SiO₂ as gate dielectric and Au/ITO as source and drain. The residual solvent was evaporated in air and then in oven at 60 °C for 1h.

Once prepared, FF:P3HT and P3HT OFETs were kept in dry box before the electrical characterization. Electrical characterization was done using a semiconductor parameter analyzer model B1500A (Agilent, USA) coupled to a probe station model 6400 (Micromanipulator Co., Carson City, USA). Fig. S6 shows polarized optical (POM) images after FF:P3HT deposition (from 1-butanol) over OFET structure.

In Fig. S7 are shown the output and transfer characteristics for P3HT FET used as reference for comparison with FF:P3HT presented in the paper. The drain current of the FET in the saturation regime is given by

\[ I_D = \frac{1}{2} \mu_{sat} C_{ox} \left( \frac{W}{L} \right) (V_{GS} - V_{th})^2 \]

Using the slope of the \( \sqrt{I_D} \) Vs. \( V_{GS} \) trace and the intersection of this curve with the x-axis, the saturation field-effect mobility, \( \mu_{FE} \), and threshold voltage, \( V_{th} \), were respectively calculated.
Figure S7. (a) Output and (b) transfer characteristics for pure P3HT FET (reference device). W/L = 500