Supporting information for:

**Photovoltaic Performance Enhancement of P3HT/PCBM Solar Cells Driven by Incorporation of Conjugated Liquid Crystalline Rod-coil Block Copolymers**

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**Synthesis of 4''-(dodecyloxy)-[1,1':4',1''-terphenyl]-4-ol (3)**

Under a dry nitrogen atmosphere, a solution of 3.6 g (13.6 mmol) of 1 in 15 mL of ethanol was added to a solution of 2.5 g of 4-(4-bromophenyl)phenol (2, 10 mmol) and 0.42 g (0.36 mmol) of Pd(PPh₃)₄ in 20 mL of toluene and 20 mL of aqueous potassium carbonate (2 M). The reaction was conducted under reflux overnight. The reaction mixture was then shaken with ethyl acetate, and the insoluble parts were filtered off. The organic layer was dried over MgSO₄, and the solvent was removed by evaporation in vacuo. The crude product was recrystallized from acetone to obtain 4''-(dodecyloxy)-[1,1':4',1''-terphenyl]-4-ol, 3. ¹H NMR (600 MHz, CDCl₃), δ (ppm): 7.73-7.65 (m, 8H), 7.53 (d, 2H), 6.93 (d, 2H), 4.91 (s, 1H), 4.05-3.98 (t, 2H), 1.96-0.61 (m, 23H).

**Synthesis of 4-(dodecyloxy)-4''-(oct-7-en-1-yloxy)-1,1':4',1''-terphenyl (terph-vinyl, A)**

1.72 g (4 mmol) of 3, 1.7 g K₂CO₃ (12 mmol), 0.66 g (4 mmol) KI dissolved in 20 mL of THF in a two-necked round bottom flask under nitrogen. Then 0.91 g (4.8 mmol) 8-bromooct-1-ene was injected. After refluxing at 80 °C overnight, the mixture was cooled and poured into water; the solution was extracted with C₂H₂Cl₂. The organic layer was dried over MgSO₄ and filtered. After solvent evaporated, the residue was purified by silica-gel chromatography. ¹H NMR (600 MHz, CDCl₃), δ (ppm): 7.56-
7.61 (m, 8H), 6.98 (d, 4H), 5.83 (m, 1H), 4.98 (d, 2H), 4.00 (t, 4H), 2.24-1.95 (m, 2H), 1.76 (d, 4H), 1.54-1.13 (m, 24H), 1.18-0.82 (m, 3H).

**Synthesis of 2-hexyloxyphenol (5) and 1,2-di(hexyloxy)benzene (6)**

5.49 g (50 mmol) of pyrocatechol (4), 12.01 g (73 mmol) of 1-bromohexane, 20.77 g (0.15 mol) of anhydrous K$_2$CO$_3$ and 0.65 g (3.6 mmol) of KI were dissolved in 100 mL of anhydrous ethanol. The solution was stirred and under reflux for 24 h. The mixture solution was filtered after cooled to room temperature. The solvent was removed and the residue was washed with diluted hydrochloric acid and brine, exacted with C$_2$H$_2$Cl$_2$ and dried with anhydrous MgSO$_4$. The crude product was purified by silica-gel column chromatography, producing 3.62 g of 2-hexyloxyphenol (5) and 7.83 g of 1,2-di(hexyloxy)benzene (6).

2-hexyloxyphenol: $^1$H NMR (600 MHz, CDCl$_3$), $\delta$ (ppm): 6.91 (m, 1H), 6.82 (m, 3H), 5.73 (s, 1H), 3.98 (t, 2H), 1.77 (m, 2H), 1.45 (m, 2H), 1.33 (m, 4H), 0.91 (t, 3H).

1,2-di(hexyloxy) benzene: $^1$H NMR (600 MHz, CDCl$_3$), $\delta$ (ppm): 6.88 (s, 4H), 3.98 (t, 4H), 1.81 (m, 4H), 1.44 (m, 4H), 1.34 (m, 8H), 0.91 (t, 6H).

**Synthesis of 2-hydroxy-3,6,7,10,11-penta(hexyloxy)triphenylene (7).**

3g of 2-hexyloxyphenol (5) and 7.24g of 1,2-di(hexyloxy)benzene (6) was dissolved in 30 mL of anhydrous C$_2$H$_2$Cl$_2$ in round-bottom flask. The solution was cooled with an ice-water bath and 23.3 g of anhydrous FeCl$_3$ was added in portion-wise in 30 min under vigorous stirring. After that, the solution was stirred at room temperature for 1 hour and cooled to 0 °C again. Then 15 mL of cold methanol was slowly added, after stirring for 30 min, 80 mL of water was added and the mixture was extracted with 300 mL of C$_2$H$_2$Cl$_2$ three times. The organic phase was collected and dried with anhydrous MgSO$_4$. After solvent was removed, the crude product was purified by silica-gel column chromatography, using petroleum ether/C$_2$H$_2$Cl$_2$ (1:15 v/v) mixture as eluent. 1.8 g of 2-hydroxy-3,6,7,10,11-penta(hexyloxy)triphenylene (7) was obtained as white crystals.

$^1$H NMR (600 MHz, CDCl$_3$), $\delta$ (ppm): 7.96 (s, 1H), 7.82 (m, 4H), 7.77 (s, 1H), 5.92
(s, 1H), 4.28-4.23 (m, 10H), 1.93 (m, 10H), 1.56 (m, 10H), 1.38 (m, 20H), 0.93 (t, 15H).

**Synthesis of 2,3,6,7,10-pentakis(hexyloxy)-11-(oct-7-en-1-yloxy)triphenylene (TP-vinyl, B)**

1.5g (1.5 mmol) of 2-hydroxy-3,6,7,10,11-penta(hexyloxy)triphenylene and 0.62 g (4.5 mmol) of anhydrous K$_2$CO$_3$ and 0.75 g (4.5 mmol) of KI were dissolved in 30 mL of DMF in a two-necked round bottom flask under nitrogen. Then 0.35 g (1.8 mmol) 8-bromooct-1-ene was injected. After refluxing at 80 °C for 24 h, the mixture was cooled and poured into water; the solution was extracted with C$_2$H$_2$Cl$_2$. The organic layer was dried with anhydrous MgSO$_4$ and filtered. After solvent evaporated, the residue was purified by silica-gel chromatography. Recrystallization from ethanol. $^1$H NMR (600 MHz, CDCl$_3$), δ (ppm): 7.83 (s, 6H), 5.82 (m, 1H), 5.10-4.87 (m, 2H), 4.21 (m, 12H), 2.08 (m, 2H), 1.92-1.85 (m, 12H), 1.56-1.36 (m, 36H), 0.93 (t, 15H).

**Synthesis of vinyl terminated P3HT (P3HT-vinyl)**

A dry 250 mL three-neck flask was flushed with N$_2$ and was charged with 2,5-dibromo-3-hexylthiophene (9.8 g, 30 mmol) and anhydrous THF (150 mL). A 2 M solution of butyl magnesium chloride (15 mL, 30 mmol) in diethyl ether (Et$_2$O) was injected via a syringe, and the reaction mixture was refluxed for 90 min. The reaction mixture was cool down to room temperature, at which time Ni(dppp)Cl$_2$ (0.3 g, 0.55 mmol) was added to the mixture solution. The polymerization was allowed to proceed for 30 min at room temperature followed by the addition of a 1 M solution of vinyl magnesium bromide (6 mL, 6 mmol). The reaction mixture was stirred for 5 min followed by quenching in methanol. The polymer was purified by sequential Soxhlet extractions with methanol, hexanes, and chloroform. The polymer was isolated from the chloroform solution. Polymer was characterized by $^1$H NMR. Molecular weight of the polymers was determined by gel permeation chromatography (GPC) Mw = 11000.
\[^{1}\text{H NMR (600 MHz, CDCl\textsubscript{3})}: \delta_{\text{H}} 6.98 (s, 1H), 6.61 (t, 1H), 5.52 (d, 2H), 5.13 (d, 2H), 2.80 (t, 2H), 1.66 (t, 2H), 1.35-1.41 (m, 6H), 0.91 (t, 3H).\]

**Synthesis of hydroxy terminated P3HT (P3HT-OH)**

Vinyl terminated P3HT (2.2 g, 0.2 mmol,) was dissolved in anhydrous THF (25 mL) under N\textsubscript{2}. To this reaction mixture, a 0.5 M solution of 9-BBN (4 mL, 2 mmol) in anhydrous THF was added via a syringe. The reaction mixture was stirred for 24 h at 40 °C, at which point a 6 M solution of NaOH (2 mL) was added to the reaction flask. The reaction mixture was stirred for another 15 min (at which point the oil bath was removed). The reaction mixture was allowed to cool down to room temperature followed by addition of a 33% aqueous solution of H\textsubscript{2}O\textsubscript{2} (2 mL), and the reaction was allowed to proceed for additional 24 h at 40 °C. The P3HT-OH was isolated by precipitation in a methanol-water mixture.

\[^{1}\text{H NMR (600 MHz, CDCl\textsubscript{3})}: \delta_{\text{H}} 6.98 (s, 1H), 3.72 (t, 2H), 3.21 (t, 2H), 2.69 (t, 2H), 1.62 (t, 2H), 1.35-1.43 (m, 6H), 0.91 (d, 3H).\]

**Synthesis of bromoester terminated poly(3-hexylthiophene) macroinitiator (P3HT-Br)**

P3HT-OH (2.2 g, 0.2 mmol) was dissolved in anhydrous THF (25 mL) under N\textsubscript{2}. The reaction mixture was stirred for 15 min at 40 °C followed by addition of triethylamine (18 mL, 132 mmol) and a drop-wise addition of 2-bromoisobutyrate bromide (15 mL, 120 mmol). The reaction mixture was stirred for 24 h at 40 °C. The resulting P3HT-Br macroinitiator was precipitated in methanol. Formation of P3HT-Br was also confirmed by \(^{1}\text{HNMR}.

\[^{1}\text{H NMR (600 MHz, CDCl\textsubscript{3})}: \delta_{\text{H}} 6.98 (s, 1H), 4.22 (t, 2H), 3.19 (s, 6H), 3.15 (t, 2H), 1.70 (s, 6H), 1.35-1.41 (m, 6H), 0.91 (t, 3H).\]
Scheme S1. Synthesis of terph-vinyl and TP-vinyl.
Figure S1. $^1$H NMR spectrum of (a) P3HT-b-Pterph and (b) P3HT-b-PTP.
Figure S2. $^1$HNMR spectrum of terph-vinyl.

Figure S3. $^1$HNMR spectrum of TP-vinyl.
**Figure S4.** TG thermograms of P3HT-\textit{b}-Pterph and P3HT-\textit{b}-PTP under nitrogen at a heating rate of 10 °C/min.

**Figure S5.** Differential scanning calorimetry (DSC) scans for P3HT-\textit{b}-Pterph and P3HT-\textit{b}-PTP during a second heating at a rate of 5 °C/min.
Figure S6. Absorbance spectra of P3HT-\(b\)-Pterph and P3HT-\(b\)-PTP.
Figure S10. Fluorescence spectra for (a) pristine P3HT-b-Pterph and P3HT-b-PTP/PCBM (b) pristine P3HT-b-Pterph and P3HT-b-PTP/PCBM films before and after annealing at different temperatures under N₂ atmosphere. (monitored at $\lambda_{\text{exc}} = 460$ nm)
Figure S7. Cyclic voltammetry (CV) plots of P3HT-b-Pterph and P3HT-b-PTP data using Ag/Ag⁺ reference. CV were performed in a three-electrode cell using platinum electrodes at a scan rate of 50 mV s⁻¹ and a Ag/Ag⁺ (0.1 M of AgNO₃ in acetonitrile) reference electrode in an anhydrous and nitrogen-saturated solution of 0.1 M tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) in acetonitrile.
Figure S8. $J-V$ characteristics of photovoltaic cells based on (a) P3HT-$b$-Pterph/PCBM (b) P3HT-$b$-PTP/PCBM films at different thermal treatments under N$_2$ atmosphere under AM 1.5G illumination from a calibrated solar simulator with an intensity of 100 mW/cm$^2$. 
Figure S9. Normalized absorbance spectra of (a) P3HT-\textit{b}\textsuperscript{-}Pterph/PCBM and (b) P3HT-\textit{b}\textsuperscript{-}PTP/PCBM films before and after annealing at different temperatures under N\textsubscript{2} atmosphere.
As cast

Annealing at 120 °C

Potoluminescence (a.u.)

Wavelength (nm)
Figure S11. Polarized photoluminescence spectra of P3HT-\textit{b}-Pterph/PCBM films before and after annealing at different temperatures under N\textsubscript{2} atmosphere. F\textsubscript{∥} is the fluorescence intensity for parallel irradiation, and F\textsubscript{⊥} is the fluorescence intensity for perpendicular irradiation.
Figure S12. Polarized photoluminescence spectra of P3HT-\textit{b}-Pterph/PCBM films before and after annealing at different temperatures under N\textsubscript{2} atmosphere. F\textsubscript{\|} is the fluorescence intensity for parallel irradiation, and F\textsubscript{\perp} is the fluorescence intensity for perpendicular irradiation.
Table S1. Dichroic data ($N_F$) of P3HT-$b$-Pterph and P3HT-$b$-PTP based active layers before and after annealing at different temperatures under N$_2$ atmosphere.

<table>
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<th>Anneal temperature (°C)(^b)</th>
<th>As cast</th>
<th>120</th>
<th>175</th>
<th>200</th>
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<tr>
<td>$N_F$</td>
<td>2.68</td>
<td>3.03</td>
<td>3.35</td>
<td>2.64</td>
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</table>

<table>
<thead>
<tr>
<th>Anneal temperature (°C)(^c)</th>
<th>As cast</th>
<th>120</th>
<th>150</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_F$</td>
<td>2.77</td>
<td>3.45</td>
<td>3.61</td>
<td>2.24</td>
</tr>
</tbody>
</table>

\(^a\) The dichroic ratios ($N$) of the active layers were determined from the polarized fluorescence spectra, using eqn. $N_F = F_{∥}/F_{⊥}$, where $N_F$ is the dichroic ratio of fluorescence, $F_{∥}$ is the fluorescence intensity for parallel irradiation, and $F_{⊥}$ is the fluorescence intensity for perpendicular irradiation. \(^b\) Active layer based on P3HT-$b$-Pterph/PCBM. \(^c\) Active layer based on P3HT-$b$-PTP/PCBM.

Figure S13. Dark $J$-$V$ characteristics of devices based on P3HT:PCBM: P3HT-$b$-PTP with various weight ratio of P3HT-$b$-PTP after annealed at 150 °C under N$_2$ atmosphere.
Figure S14. Normalized absorption spectra of P3HT:PCBM and P3HT:PCBM: P3HT-\textit{b}-Pterph films with various weight ratio of P3HT-\textit{b}-Pterph after annealed at 175 °C under N$_2$ atmosphere.
Figure S15. 5 μm × 5 μm tapping-mode AFM topography height images of P3HT:PCBM and P3HT:PCBM: P3HT-\textit{b}-Pterph films with various weight ratio of P3HT-\textit{b}-Pterph after annealed at 175 °C under N\textsubscript{2} atmosphere.
Figure S16. PL spectra of P3HT, P3HT:PCBM and P3HT:PCBM: P3HT-\textit{b}-Pterph films with various weight ratio of P3HT-\textit{b}-Pterph after annealed at 175 \degree C under N$_2$ atmosphere.