Supporting Information

Uniform Polyselenophene Block Copolymer Fiber-like Micelles and Block Co-micelles via Living Crystallization-Driven Self-Assembly

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Figure S1. $^1$H-NMR (400 MHz, CDCl$_3$) spectrum of ethynyl-capped P3DSe$_{17}$. Residual solvent peaks are marked with an *.
Figure S2. MALDI-TOF spectrum of ethynyl-capped P3DSe$_{17}$ and table of end-capping efficiency as determined by integration of the peaks using Bruker PolyTools software.

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<th>H/H / %</th>
<th>H/ethynyl / %</th>
<th>Ethynyl/ethynyl / %</th>
<th>Br/H / %</th>
<th>Br/ethynyl / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3DSe$_{17}$</td>
<td>11.1</td>
<td>23.1</td>
<td>7.9</td>
<td>11.2</td>
<td>12.5</td>
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Figure S3. GPC trace (refractive index) of bromo-terminated PDMS$_{240}$ eluted in THF (1 mL/min) at 35 °C. The low signal-to-noise ratio is due to PDMS having a similar refractive index to THF.
**Figure S4.** $^1$H-NMR (400 MHz, CDCl$_3$) of bromo-terminated PDMS$_{240}$. Residual H$_2$O and THF peaks are marked with an *. The two singlet satellites, flanking the main SiMe$_2$ peak at 0.07 ppm arise from coupling to abundant $^{29}$Si isotopes.
Figure S5. $^1$H-NMR (400 MHz, CDCl$_3$) of azide-terminated PDMS$_{240}$. Residual H$_2$O peak is marked with an *. The two singlet satellites, flanking the main SiMe$_2$ peak at 0.07 ppm arise from coupling to abundant $^{29}$Si isotopes.
Figure S6. $^1$H-NMR (400 MHz, CDCl$_3$) of P3DSe$_{17}$-b-PDMS$_{240}$. Residual CHCl$_3$, THF and H$_2$O are marked with an *.

Figure S7. GPC traces (UV response) eluted in THF (1 mL/min) at 35 °C of P3DSe$_{17}$ homopolymer (red trace) and P3DSe$_{17}$-b-PDMS$_{240}$ BCP after SEC purification (black trace).
**Figure S8.** WAXS diffraction pattern of dried P3DSe$_{17}$-PDMS$_{240}$ micelles.

**Figure S9.** WAXS diffraction pattern of an unannealed bulk sample of P3DSe$_{17}$ homopolymer.
Figure S10. Optical absorption spectra of P3DSe$_{17}$-b-PDMS$_{240}$ unimer in THF (solid line, 0.02 mg/mL) and micelles in EtOAc (dashed line, 0.02 mg/mL).

Figure S11. Photoluminescence spectra of P3DSe$_{17}$-b-PDMS$_{240}$ unimer in THF (solid line, 0.02 mg/mL) and micelles in EtOAc (dashed line, 0.02 mg/mL).
Figure S12. Bright-field TEM images of polydisperse P3DSe$_{17}$-$b$-PDMS$_{240}$ micelles self-seeded at 60 °C in EtOAc (0.5 mg/mL) which had been aged for 24 h and drop-cast onto carbon-coated copper grids. Scale bar is 1000 nm.

Scheme S1. Synthesis of P3DSe$_{17}$-$b$-PS$_{140}$. PMDETA = $N,N,N',N''$,N'''-pentamethyldiethylenetriamine.
Figure S13. GPC traces (UV response) eluted in THF (1 mL/min) at 35 °C of P3DSe\textsubscript{17-b-PDMS\textsubscript{240}} before (left) and after sonication for 1 h at 0 °C (right).

Figure S14. GPC traces (UV response) eluted in THF (1 mL/min) at 35 °C of P3DSe\textsubscript{17} homopolymer (red trace) and P3DSe\textsubscript{17-b-PS\textsubscript{140}} after SEC purification (black trace).
**Figure S15.** $^1$H-NMR (400 MHz, CDCl$_3$) of bromo-capped PS$_{140}$. Residual CHCl$_3$, THF and H$_2$O are marked with an *.

**Figure S16.** MALDI-TOF spectrum of bromo-capped PS$_{140}$. 104.15 Da
Figure S17. $^1$H-NMR (400 MHz, CDCl$_3$) of azide-capped PS$_{140}$. Residual CHCl$_3$ and H$_2$O are marked with an *.
Figure S18. $^1$H-NMR (400 MHz, CDCl$_3$) of P3DSe$_{17}$-$b$-PS$_{140}$. Residual CHCl$_3$ and H$_2$O are marked with an *.