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Supporting Information for

“Cross” Supermicelles via the Hierarchical Assembly of
Amphiphilic Cylindrical Triblock Comicelles

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Materials. Methanol, iso-propanol, n-hexane, n-butyl lithium and 2,2-dimethoxy-2-diphenylacetophenone (DMPA), benzophenone, sodium were purchased from Sigma-Aldrich and used as received. Diphenylethylene, dimethylsilacyclobutane, 2-vinyl pyridine, and tert-butyl acrylate were distilled over CaH₂ twice before use. Platinum-divinyltetramethyldisiloxane complex in xylene (Karstedt’s catalyst) with a Pt wt% of 2.1-2.4 was purchased from ABCR. Dimethyl[1] silaferrocenophane was synthesized by following a previous report. V₃ (1,3,5-trimethyl-1,3,5-trivinyleclotrisiloxane) were pre-dried with calcium hydride and distilled prior to use. Chlorodimethylvinylsilane and chlorotrimethylsilane were distilled prior to use. D₃ (hexamethylyclotrisiloxane) was dissolved in pentane and pre-dried with CaH₂ before being dried in vacuo and sublimed onto a -5 °C cold
finger. For the anionic polymerizations, THF was pre-dried with Na before being distilled over Na/benzophenone under nitrogen.

**Synthesis of the diblock copolymers.** The diblock copolymers used in this study were synthesized via living anionic polymerization in an inert atmosphere glovebox. The detailed polymerization procedures for PFS-b-PDMS, PFS-b-PMVS, PFS-b-P2VP have been reported elsewhere and will not be repeated here.\(^2\)\(^,\)\(^3\) All block copolymers together with their characteristics are listed in Table S1.

The detailed polymerization procedure for PFS-b-PtBA is described as follows (by taking PFS\(_{20}\)-b-PtBA\(_{280}\) as an example). Dimethyl[1]silaferrocenophane (121 mg, 0.5 mmol) was dissolved in 5.0 mL THF, into which \(n\)-butyl lithium (1.6 M in hexanes, 16 \(\mu\)L, 0.0256 mmol) was added. The solution was allowed to stir at room temperature for 1 h before 1.0 mL of aliquot was taken out and quenched to characterize the PFS homopolymer. The solution was cooled to -78 \(^\circ\)C, and subsequently diphenylethylene (17.5 \(\mu\)L, 0.1 mmol) and dimethylsilacyclobutane (6.5 \(\mu\)L, 0.05 mmol) were added. After stirring for another 10 min, mixture solution of \(tert\)-butyl acrylate (520 mg, 4.06 mmol in 5.0 mL THF, precooled to -78 \(^\circ\)C) and lithium chloride (10 mg) was added in one portion into the reaction solution. The polymerization was carried out for another 2 h at -78 \(^\circ\)C before 2 mg of 4-\(tert\)-butylphenol was added into the solution to quench the anion. The polymer was precipitated into mixture solvent of MeOH and water (8:2, v/v). The polymer was fractionated by size-exclusion column (using THF as eluent) to remove PFS homopolymer (yield = 85 \%). The \(^1\)H NMR spectrum of the diblock copolymer is included in Figure S6.

Fluorescent dye-labeled PFS-b-PtBA and PFS-b-P2VP were obtained by post-polymerization modification. Taking PFS\(_{20}\)-b-PtBA\(_{320}\)-D\(_R\) as an example, the PFS-b-PtBA-OH precursor with a hydroxyl terminal group was synthesized by terminating the anionic polymerization of PFS-b-PtBA with ethylene oxide (3 equiv.) and subsequently reacting with 4-\(tert\)-butylphenol (functionalization degree = 99\% by \(^1\)H NMR). Typically, the red dye (BODIPY 630/650, 3 mg, 8\(\times\)10\(^{-3}\) mmol of carboxyl groups) was mixed with 80 mg of the PFS-b-PtBA-OH with a hydroxyl terminal
group \((2 \times 10^{-3} \text{ mmol of hydroxyl groups})\), 1 mg of dicyclohexylcarbodiimide \((8 \times 10^{-3} \text{ mmol})\) and 0.8 mg of 4-dimethylaminopyridine \((1 \times 10^{-3} \text{ mmol})\) in dry THF. The mixture solution was stirred at room temperature for 3 days before the polymer was precipitated into mixture solvent of MeOH and water \((8:2, \text{ v/v})\) for 3 times and excess amount of dyes were removed completely by dialysis against THF (functionalization degree = 95\% by \(^1\)H NMR, yield = 80\%). The green dye-containing polymer was prepared the same way except that the green dye BODIPY-FL was used.

**Polymer characterization.** Gel permeation chromatography (GPC) was carried out on a Viscotek VE 2001 Triple-Detector Gel Permeation Chromatograph equipped with an automatic sampler, a pump, an injector, an inline degasser, and a column oven (30 °C). The elution columns consist of styrene/divinyl benzene gels with pore sizes of 500 Å and 100,000 Å. Detection was conducted by means of a VE 3580 refractometer, a four-capillary differential viscometer, and 90° and low angle (7°) laser light \((\lambda_0 = 670 \text{ nm})\) scattering detectors, VE 3210 & VE 270. THF (Fisher) was used as the eluent, with a flow rate of 1.0 mL/min. Samples were dissolved in the eluent (2 mg/mL) and filtered with a Ministart SRP 15 filter (polytetrafluoroethylene membrane of 0.45 \(\mu\)m pore size) before analysis. The calibration was conducted using a PolyCALTM polystyrene standard from Viscotek. To determine the molar mass of the block copolymers, aliquots of the first block were taken and the molar mass of the first block was determined by GPC. The polymerization degrees of the two blocks were then determined by combining the molecular weight \(M_n\) of the first block with the block ratio of the diblock copolymer which was obtained by integration of the \(^1\)H NMR spectrum.

**Preparation of seed cylinders.** Seed cylinders were prepared by ultrasonication of the block copolymer cylinders in a selective solvent at low temperature. The polydisperse cylinder precursors were obtained by directly dispersing the diblock copolymers into the selective solvent and heated at 80 °C for 1 h before the solution was allowed to cool down gradually to room temperature. Then, the cylinders were sonicated (50W sonication processor equipped with a titanium sonotrode) at -78 °C for 1 h. The lengths of seed cylinders could be increased by adding more unimers (the
polymer dissolved in THF) into the existing seed micelle solution.4–6

**Preparation of triblock micelles.** The triblock micelles were prepared via seeded growth. Taking triblock micelle $P$-$H$-$P$ (M(PFS$_{20}$-$b$-PtBA$_{280}$)-$b$-M(PFS$_{28}$-$b$-PDMS$_{560}$)-$b$-M(PFS$_{20}$-$b$-PtBA$_{280}$)) for example. Into the $n$-hexane solution of PFS$_{28}$-$b$-PDMS$_{560}$ seed cylinders (1.0 mL, 0.025 mg/mL), 4.0 mL of $i$-PrOH was added with stirring and certain amount of PFS$_{20}$-$b$-PtBA$_{280}$ unimers in THF (10 mg/mL) was added to achieve desired cylinder length. After stirring at 500 rpm for 30 seconds, the solution was kept still for at least 12 h before being analyzed by TEM.

**Preparation of supermicelles via hydrophobic interactions.** Taking triblock micelle $P$-$H$-$P$ (M(PFS$_{20}$-$b$-PtBA$_{280}$)-$b$-M(PFS$_{28}$-$b$-PDMS$_{560}$)-$b$-M(PFS$_{20}$-$b$-PtBA$_{280}$)) for example. The triblock micelles were dispersed in mixture solvent of $n$-hexane : $i$-PrOH = 1 : 4, v/v initially. The solvent was slowly switched to MeOH by changing the solvent stepwise via dialysis ($i$-PrOH, $i$-PrOH : MeOH = 8:2, 6:4, 4:6, 2:8 and eventually MeOH). This slow solvent switching protocol was designed to gradually induce the aggregation of insoluble block and thus the formation of supermicelles.

**Preparation of fluorescent “cross” supermicelles.** To demonstrate that “cross” supermicelles actually form in solution rather than simply on drying on a TEM grid a sample of triblock micelles was aggregated in a selective solvent for the end segments and the resulting structures were then processed, functionalized, and characterised in solution by LSCM without solvent removal (except for aliquots removed for comparative TEM analysis).

First, “cross” supermicelles were obtained by dispersing $P’$-$H’$-$P’$ triblock micelles (M(PFS$_{25}$-$b$-P2VP$_{250}$)-$b$-M(PFS$_{36}$-$b$-PMVS$_{324}$)-$b$-M(PFS$_{25}$-$b$-P2VP$_{250}$)) in MeOH. Next, without any prior solvent removal, the “cross” supermicelles were crosslinked in solution through their H’ cores. The MeOH solution (1.0 mL) was degassed by N$_2$ bubbling for 30 min before being transferred into glovebox (Argon atmosphere), in which 10 µL of DMPA photoinitiator in MeOH solution (10 mg/mL) was added. The solution was subsequently subjected to UV-irradiation for 30 min
with occasional agitation. The collapsed and densely packed PMVS chains were crosslinked upon UV-irradiation. The solvent was subsequently switched to i-PrOH via dialysis, since MeOH is not an ideal solvent for CDSA. The fluorescent “cross” supermicelles were prepared by simply growing M(PFS$_{20}$-$b$-PtBA$_{320}$-$D_R$) (end-labeled with the red-dye BODIPY 630/650) segments at the ends of core-crosslinked “cross” supermicelles. Thus 1 µL of PFS$_{20}$-$b$-PtBA$_{320}$-$D_R$ THF solution (10 mg/mL) was added into the solution to grow the fluorescent segments. The solution was kept still for at least 12 h before being analyzed by LCSM. To prepare the block “cross” supermicelles, another 2 µL of PFS$_{27}$-$b$-P2VP$_{520}$-$D_G$ THF solution (10 mg/mL) was added into the solution.

**Preparation of cylindrical micelles from PFS$_{20}$-$b$-PtBA$_{170}$**. The initial cylinders were obtained by directly dispersing the diblock copolymer into i-PrOH and heating at 80 °C for 1 h before the solution was allowed to cool down naturally to room temperature. Then, the cylinders were sonicated at 0 °C for 1 h. The lengths of the seed cylinders could be increased by adding more unimers (the polymer dissolved in THF) into the existing seed micelle solution.$^{4-6}$

**Laser scanning confocal microscopy (LSCM)**. Confocal imaging was performed using a Leica SP5 system attached to a Leica DMI6000 inverted epifluorescence microscope with a ×63 (numerical aperture 1.4) oil immersion objective lens. Fluorophores from PFS$_{20}$-$b$-PtBA$_{320}$-$D_R$ were excited using a HeNe laser operating at 594 nm, and those from PFS$_{27}$-$b$-P2VP$_{520}$-$D_G$ were excited using an argon laser operating at 488 nm. Confocal images were obtained using digital detectors with observation windows of 605–700 nm for $D_R$ and 500–570 nm for $D_G$. The resulting outputs were obtained as digital false-color images, and were color coded as red and green, respectively. Micelle concentrations of 0.01 mg ml$^{-1}$ in i-PrOH were used for imaging experiments.

**General characterization techniques**. Transmission electron microscopy (TEM) samples were prepared by drop-casting one drop (ca. 10 µL) of the solution onto a carbon-coated copper grid which was placed on a piece of filter paper to remove excess solvent. Bright field TEM images were obtained on a JEOL1200EX II
microscope operating at 120 kV and equipped with an SIS MegaViewIII digital camera. No staining of the samples was necessary. Images were analyzed using the ImageJ software package developed at the US National Institute of Health for the statistical length analysis.

Micelle length distributions were determined using the software program ImageJ from the U.S. National Institutes of Health. For each sample, ca. 100 micelles in several images were traced by hand in order to obtain the length information. The number average micelle length \((L_n)\) and weight average micelle length \((L_w)\) were calculated using eq. S1 and eq. S2 from measurements of the contour lengths \((L_i)\) of individual micelles, where \(N_i\) is the number of micelles of length \(L_i\), and \(n\) is the number of micelles examined in each sample.

\[
L_n = \frac{\sum_{i=1}^{n} N_i L_i}{\sum_{i=1}^{n} N_i}
\]  \hspace{1cm} (S1)

\[
L_w = \frac{\sum_{i=1}^{n} N_i L_i^2}{\sum_{i=1}^{n} N_i L_i}
\]  \hspace{1cm} (S2)

The distribution of micelle lengths is characterized by both \(L_w / L_n\) and the standard deviation of the length distribution \(\sigma\).

Dynamic light scattering (173°) experiments were performed using a nano series Malvern zetasizer instrument equipped with a 633 nm red laser. Samples were analyzed in 1 cm glass cuvettes at 25 °C. For the purpose of the light scattering studies, the refractive index of the block copolymers involved was assumed to be 1.60. The results of dynamic light scattering studies are reported as apparent hydrodynamic radius \((R_{h, \text{app}})\), acknowledging that the particles have been modelled as hard spheres in the experiments conducted.

All of the \(^1\text{H} \) NMR characterization was carried out on a Varian 500 MHz instrument, with chemical shifts referenced to tetramethylsilane (TMS) in \(d\)-chloroform (CDCl\(_3\)).
Atomic force microscopy (AFM). Atomic force microscopy (AFM) images were obtained in ambient conditions utilizing a Multimode VIII with a Nanoscope V controller with PeakForce feedback control. The micelle samples were prepared by drop-casting 0.05 mg/mL solution of micelles onto freshly cleaved highly ordered pyrolytic graphite (HOPG). All AFM images from which dimensions were determined were obtained with a fresh SCANASYST-HR (Bruker) cantilever of nominal tip radius 2 nm. The dimensions quoted in the text have not been corrected for tip effects, which are expected to be negligible. Images were analyzed using Gwyddion, an open source software program for SPM images (www.gwyddion.net).

Small-angle X-ray scattering. The X-ray diffraction data was taken with a Ganesha small angle X-ray scattering apparatus (SAXSLAB, Denmark). The instrument uses copper Kα radiation (1.5 Å) and the scattering pattern is detected on a 2-dimensional Pilatus 300K X-Ray Detector (Dectris, Switzerland). The detector was positioned at a distance of approximately 1400 mm away from the sample. Samples were prepared at 5 mg/mL and 8 mg/mL and sealed into 1.5 mm diameter quartz capillary tubes (Capillary Tube Supplies, Cornwall, UK). The instrument was evacuated during measurements to reduce air scattering.

In order to determine the cross-sectional dimensions of the core regions of the cylindrical micelles (PFS$_{20}$-b-PtBA$_{280}$, $L_n = 810$ nm, $L_w/L_n$ of 1.08) in solution, a small-angle scattering experiment was performed on micelle dispersions in isopropanol. At the concentrations investigated, 5 mg/mL and 8 mg/mL, the samples exhibited isotropic scattering with no apparent contributions from inter-particle interactions. The intensity as a function of scattering vector Q could therefore be analyzed using a previously described model for the scattering from a cylindrical core-shell micelle with a corona of decaying density. The background subtracted data and correspond model fits are shown in Figure S7 and at both concentrations showed an average core radius of 3.8 ± 0.2 nm. These values are in good agreement with previously measured PFS-based micelles. In both datasets there is a slight deviation from the model at scattering vectors close to 0.1 Å$^{-1}$, this can been ascribed to interactions between corona chains which will be dependent on both the solvent
and the chemical composition of the corona chains. Such interactions are not included in the model, however it was established that the presence of these discrepancies does not affect the results for the core and corona radii.

**Quaternization of the “cross” supermicelles formed by P’-H-P’ triblock comicelles.** Into the MeOH solution of “cross” supermicelles was added a large excess amount of CH$_3$I (molar ratio of CH$_3$I : pyridyl groups > 1000 : 1). The solution was allowed to stay still overnight and excess amount of CH$_3$I was removed by dialysis against MeOH before TEM characterization.

Due to the low concentration of supermicelles in solution, quantitative characterization of their degree of quaternization was not obtained. However, based on literature descriptions of the same transformations,$^7,8$ with a high ratio of CH$_3$I : pyridyl groups (> 1000 : 1), a degree of quaternization for the P2VP chains of at least ca. 80 % would be anticipated. The quaternization of P2VP chains was expected to lead to an expansion of the chain dimensions (from both electrostatic repulsion and steric hindrance).$^9,10$

To explore the effect of quaternization of P2VP in MeOH, the hydrodynamic diameter of quaternized (q) qP2VP$_{200}$ homopolymer was measured via DLS, and the result was compared with the value for the neutral P2VP$_{200}$ homopolymer. An apparent hydrodynamic diameter of 9.2 nm was obtained for the P2VP$_{200}$ homopolymer (which was prepared by anionic polymerization with a PDI of 1.07), and a value of 10.7 nm, representing an expanded coil, was obtained for the qP2VP.

**Discussion of the relationship between $L_2$ and the DP value for PtBA in cylindrical micelles formed by PFS-$b$-PtBA diblock copolymers.** To provide an estimate of the coronal PtBA chain length in solution, we considered the PFS-$b$-PtBA cylindrical micelles as a layer of PtBA polymer brush chains grafted on the surface of PFS cylindrical core. The grafting density of coronal PtBA chains on the PFS cylindrical core can be calculated.

Taking PFS$_{30}$-$b$-PtBA$_{600}$ for example:

The number of PtBA chains ($N_{PtBA}$) on a cylindrical micelle with a length of L assuming circular cross-section can be calculated as:
\[ N_{\text{PtBA}} = N_{\text{PFS}} = \frac{m_{\text{PFS}}}{M_{\text{PFS}}} N_A = \frac{\rho_{\text{PFS}} \times \nu_{\text{PFS}}}{D_P \times P_{\text{core}} \times M_{\text{monomer}}} N_A = \frac{\rho_{\text{PFS}} \times \pi r^2 L}{D_P \times P_{\text{core}} \times M_{\text{monomer}}} N_A \] (3)

where \( m_{\text{PFS}} \) is the mass of PFS, \( M_{\text{PFS}} \) is the mass of PFS in a single micelle, \( N_A \) is the Avogadro constant, \( \rho_{\text{PFS}} = 1.3 \text{ g/cm}^3 \); \( r \) the core radius of the cylindrical micelles from this polymer is 3.8 nm, as obtained from our SAXS experiments described above (see Figure S7);\(^{12,13}\) \( D_P = 30 \) and \( M_{\text{monomer}} = 242 \text{ g/mol} \). From Eq. 3, we can estimate \( N_{\text{PtBA}} \) to be \( 4.6 \times 10^9 \times L/m \), comparable to the value we found previously with light scattering for related micelles with a polyisoprene corona.\(^{14}\)

The grafting density (\( D_G \)) of PtBA chains is
\[ D_G = \frac{N_{\text{PtBA}}}{A_{\text{cor}}} = \frac{N_{\text{PtBA}}}{2\pi r L} \] (4)

where \( A_{\text{cor}} \) is the surface area of the PFS core.

Inserting \( N_{\text{PtBA}} \) into Eq. 4, we can estimate the grafting density of PtBA chains as 0.20 chain/nm\(^2\). This grafting density suggests that the PtBA chains are in the “concentrated polymer brush (CPB)” regime (\( >0.1 \text{ chain/nm}^2 \)),\(^{15-17}\) where higher-order segmental interactions and the non-Gaussian nature of stretched chains become important. Furthermore, for cylindrical micelles from other PFS-\( b \)-PtBA BCPs, the same assumptions can be applied, and their values of \( D_G \) should be similar.

When polymer chains densely grafted onto an impenetrable surface are immersed in a good solvent, the excluded volume effects strongly stretch the chains and they form a blob structure.\(^{18-20}\) As proposed by Borisov and coworkers for a dense cylindrical polymer brush in a good solvent, the hydrodynamic thickness of the brush layer is proportional to \( D_P \times P_{\text{corona}}^{0.75} \) (which changes to \( D_P \times P_{\text{corona}}^{0.80} \) for short chains on a spherical surface) and to \( D_P \times P_{\text{corona}}^{0.67} \) in a \( \theta \) solvent.\(^{18-20}\) Thus, the thickness of the corona layer or the length of the corona chains (\( L_2 \)) should be approximately proportional to \( D_P^{0.5-0.8} \) depending on the quality of solvent.

In this paper, we use the DP value for the PtBA (or P2VP) corona chains to characterize \( L_2 \) (or \( L_2' \)) with respect to the self-assembly behavior of the triblock comicelles as DP is a more commonly used characteristic for polymers (see Figure 5(E) and Scheme 3(A)).
Scheme S1. The molecular structures of the diblock copolymers used in this study.

Table S1. Characterisation of the block copolymers used in this study.

| Mn (kDa) a | Mw / Mn b | block ratio b |
|-----------|-----------|--------------|
| PFS28-b-PDMS560 | 48.2 | 1.02 | 1:20 |
| PFS36-b-PMVS324 | 37.8 | 1.10 | 1:9 |
| PFS21-b-PtBA170 | 27.1 | 1.16 | 1:8.1 |
| PFS20-b-PtBA280 | 41.1 | 1.09 | 1:14 |
| PFS20-b-PtBA320-DR | 46.4 | 1.18 | 1:16 |
| PFS32-b-PtBA460 | 49.6 | 1.20 | 1:14.4 |
| PFS30-b-PtBA600 | 74.1 | 1.17 | 1:20 |
| PFS25-b-P2VP250 | 19.9 | 1.09 | 1:10 |
| PFS32-b-P2VP760 | 71.8 | 1.05 | 1:23.8 |
| PFS27-b-P2VP520-DG | 61.6 | 1.09 | 1:19.2 |

a: These values were determined via GPC, using THF as eluent and polystyrene as standard. The polymerization degrees of the PFS blocks were determined from their corresponding PFS homopolymers; b: the block ratios were obtained from the 1H NMR spectra of these polymers and the degree of polymerization of the second block were determined by combining the MALDI-TOF results of the PFS homopolymers and 1H NMR integration of the diblock copolymers.

Table S2. Characterisation of the seed cylinders a

| L1 | Lw (nm) | Ln (nm) | Lw / Ln | σ (nm) |
|----|--------|--------|--------|--------|
| H seeds (16 nm) | 16.4 | 15.9 | 1.03 | 2.9 |
| H seeds (27 nm) | 27.7 | 26.9 | 1.03 | 4.9 |
| H seeds (37 nm) | 38.2 | 36.7 | 1.04 | 7.2 |
| H seeds (56 nm) | 58.7 | 56.4 | 1.04 | 11.2 |
| H’ seeds (20 nm) | 23.3 | 20.1 | 1.16 | 8.0 |

a: the lengths of the cylinders were measured from their TEM images and the values were obtained by averaging over a sample size of 100. H seeds were prepared from PFS28-b-PDMS560, and H’ seeds were prepared from PFS36-b-PMVS324.
Table S3. Characterisation of the amphiphilic triblock comicelles\textsuperscript{a}

|                  | \(L_n\) (nm) | \(L_w\) (nm) | \(L_w / L_n\) | \(\sigma\) (nm) |
|------------------|--------------|--------------|---------------|---------------|
| **P-H-P triblock comicelles** |              |              |               |               |
| \(L_1 = 16\) nm, \(DP_2 = 170\) | 428          | 437          | 1.02          | 61            |
| \(DP_2 = 280\) | 557          | 568          | 1.02          | 79            |
| \(DP_2 = 460\) | 841          | 866          | 1.03          | 146           |
| \(DP_2 = 600\) | 683          | 697          | 1.02          | 97            |
| \(L_1 = 27\) nm, \(DP_2 = 170\) | 427          | 440          | 1.03          | 74            |
| \(DP_2 = 280\) | 580          | 597          | 1.03          | 100           |
| \(DP_2 = 460\) | 642          | 655          | 1.02          | 91            |
| \(DP_2 = 600\) | 604          | 610          | 1.01          | 60            |
| \(L_1 = 37\) nm, \(DP_2 = 170\) | 660          | 673          | 1.02          | 93            |
| \(DP_2 = 280\) | 614          | 626          | 1.02          | 87            |
| \(DP_2 = 460\) | 620          | 639          | 1.03          | 107           |
| \(DP_2 = 600\) | 725          | 732          | 1.01          | 73            |
| \(L_1 = 56\) nm, \(DP_2 = 170\) | 402          | 410          | 1.02          | 57            |
| \(DP_2 = 280\) | 396          | 408          | 1.03          | 69            |
| \(DP_2 = 460\) | 494          | 504          | 1.02          | 70            |
| \(DP_2 = 600\) | 447          | 456          | 1.02          | 63            |
| **P’-H-P’ triblock comicelles** |              |              |               |               |
| \(L_1 = 16\) nm, \(DP_2’ = 250\) | 484          | 497          | 1.02          | 68            |
| \(DP_2’ = 760\) | 388          | 398          | 1.02          | 55            |
| **P’-H’-P’ triblock comicelles** |              |              |               |               |
| \(L_1’ = 20\) nm, \(DP_2’ = 250\) | 756          | 771          | 1.02          | 107           |

\textsuperscript{a} the lengths of the cylinders were measured from their TEM images and the values were obtained by averaging over 100 readings. H seeds are prepared from PFS\textsubscript{28-b-PDMS\textsubscript{560}}, H’ seeds are prepared from PFS\textsubscript{36-b-PMVS\textsubscript{324}}; P segments are prepared from PFS-b-PtBA polymers and P’ segments are from PFS-b-P2VP polymers.

\textsuperscript{b} \(DP_2\) is the DP of the corona-forming block from P or P’ segments.
Figure S1. Representative TEM images of the P-H-P triblock micelles with different central H segment lengths ($L_1$) and degrees of polymerization of the PtBA chain ($DP_2$) of the two end P segments (related to $L_2$). The cylinders were dispersed in $n$-hexane : $i$-PrOH = 1 : 4. The images in bottom row are the corresponding H seed cylinders dispersed in $n$-hexane. Scale bars are 1 µm for the triblock micelles and 500 nm for the seed cylinders.
Figure S2. Representative TEM images of the supermicelles formed in MeOH (after solvent evaporation) from the P-H-P triblock comicles with different values for $L_1$ and the degree of polymerization of the PtBA chains of the two end P segments (DP$_2$, related to $L_2$). Scale bars are 500 nm.

Figure S3. (A) TEM image of the cylindrical micelles from PFS$_{20}$-b-PtBA$_{170}$ ($L_n = 510$ nm and PDI = 1.14, scale bar is 500 nm) in MeOH; and (B) the normalized DLS data of the cylindrical micelles in $i$-PrOH and MeOH.
Figure S4. TEM images of triblock comicelles in $n$-hexane : $i$-PrOH = 1: 4, (A) $P'$-H-$P'$ ($L_1 = 16$ nm, DP$_2'$ = 760); (B) $P'$-H-$P'$ ($L_1 = 16$ nm, DP$_2'$ = 250); (C) $P'$-H'-P' ($L_1' = 20$ nm, DP$_2'$ = 250). Image (D) shows triblock comicelles $P'$-H-$P'$ ($L_1 = 15$ nm, DP$_2'$ = 760) in MeOH. Scale bars are 1 $\mu$m.

Figure S5. Low-resolution TEM images of the “cross” supermicelles from $P'$-H'-P’$ triblock comicelles (see Table S3 for details) in MeOH. The fluorescent “cross” supermicelles were prepared from these supermicelles. Scale bar is 2 $\mu$m.
Figure S6. $^1$H NMR spectrum of PFS$_{20}$-b-PtBA$_{280}$ (obtained in CDCl$_3$).

The peak at 1.6 ppm probably includes a contribution from water.

Figure S7. Azimuthally averaged intensity from SAXS from the cylindrical micelles of PFS$_{20}$-b-PtBA$_{280}$ in i-PrOH. The intensity data from the 8 mg / mL has been multiplied by a factor of 10 for clarity.

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