

**Electronic Supplementary Information**

**Multicompartment micelles from a metallo-supramolecular  
tetrablock quatercopolymer**

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## 1. Synthesis and characterization of the PTFMS<sub>20</sub>-*b*-PtBA<sub>25</sub>-*b*-PS<sub>35</sub>-[Ru]-PEG<sub>70</sub> tetrablock quaterpolymer

### ]-PS<sub>35</sub> and ]-PtBA<sub>25</sub>-*b*-PS<sub>35</sub>

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### ]-PS<sub>35</sub>-*b*-PtBA<sub>25</sub>-*b*-PTFMS<sub>20</sub>

The poly(styrene-*b*-*t*-butyl acrylate) macroinitiator (150 mg,  $1.1 \times 10^{-5}$  mol,  $M_n = 7,400$  g/mol, PDI = 1.15) was dissolved in purified *para*-trifluoromethylstyrene (530 mg, 3.0 mmol, M/I = 150). Three freeze-pump-thaw cycles were applied, and the reaction mixture was heated for 2.5 hours at 120 °C. The block copolymer was precipitated twice from dichloromethane into methanol. The precipitate was collected and dried under vacuum to yield the desired block copolymer. <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) = 8.68 (m, 2 H; H<sub>6,6''</sub>), 8.65 (m, 2 H; H<sub>3,3''</sub>), 8.13 (m, 2 H; H<sub>3',5'</sub>), 7.89 (m, 2 H; H<sub>4,4''</sub>), 7.45-6.35 (m, 266 H; H<sub>PS backbone, H<sub>aromatic, H<sub>5,5''</sub></sub>), 5.30-5.20 (m, 2 H; tpyOCH<sub>2</sub>), 4.78 (m, 1 H; HC-ON, both diastereomers), 3.54-3.20 (m, 1H; ON-CH, major & minor), 2.90-0.41 (m, 586 H; H<sub>PTFMS & PS & PtBA backbone, CH<sub>3</sub>CHCH<sub>3</sub> major, C(CH<sub>3</sub>)<sub>3</sub>; CH<sub>3</sub>CHCH<sub>3</sub> minor, CH<sub>3</sub>CHCH<sub>3</sub>; CH<sub>3</sub>CH-ON). GPC (eluent DMA with LiCl 2.1 g/L):  $M_n = 8,700$  g/mol, PDI = 1.33.</sub></sub>

### PTFMS<sub>20</sub>-*b*-PtBA<sub>25</sub>-*b*-PS<sub>35</sub>-[Ru]-PEG<sub>70</sub>

PEG<sub>70</sub>-[RuCl<sub>3</sub> and the terpyridine-functionalized polymer were dissolved in a degassed mixture of or CHCl<sub>3</sub>:MeOH. Subsequently, the reaction mixture was heated to 85 °C for 30 minutes. A few drops of *N*-ethylmorpholine were added to the solution. Stirring under reflux was continued overnight, after which an excess of NH<sub>4</sub>PF<sub>6</sub> was added. The solvent was removed *in vacuo* and the reaction mixture was partitioned between 25 mL water and 25 mL methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>). The organic layer was washed with water (3 × 25 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and finally

removed *in vacuo*. The metallo-supramolecular block copolymer was further purified by preparative size exclusion chromatography (BioBeads SX-1) and column chromatography ( $\text{Al}_2\text{O}_3$ ).

$\text{PEG}_{70}$ - $[\text{RuCl}_3]$  (30 mg,  $M_n = 3,400$  g/mol, PDI = 1.07) and the terpyridine-functionalized  $\text{PTFMS}_{20}$ -*block*-*PtBA* $_{25}$ -*block*- $\text{PS}_{35}$ - $[\text{Ru}]$  (67 mg,  $M_n = 10,900$  g/mol, PDI = 1.33) were dissolved in a mixture of 0.6 mL  $\text{CHCl}_3$  and 0.3 mL MeOH.  $^1\text{H-NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$ (ppm) = 8.62-8.37 (m, 8H;  $\text{H}_{3':5'}$ ,  $\text{H}_{3:3''}$ ), 7.86 (m, 4H;  $\text{H}_{4:4''}$ ), 7.45-6.35 (m, 272 H;  $\text{H}_{\text{PS}} \& \text{PTFMS}$  aromatic backbone,  $\text{H}_{\text{aromatic}}$ ,  $\text{H}_{6,6''}$ ,  $\text{H}_{5,5''}$ ), 5.30-5.20 (m, 2 H;  $\text{tpyOCH}_2$ ), 4.78 (m, 1 H;  $\text{HC-ON}$ , both diastereomers), 3.90-3.15 (m, 281 H;  $\text{ON-CH}$ , major & minor,  $\text{OCH}_2$  PEG backbone), 2.90-0.41 (m, 586 H;  $\text{H}_{\text{PTFMS}} \& \text{PS} \& \text{PtBA}$  backbone,  $\text{CH}_3\text{CHCH}_3$  major,  $\text{C}(\text{CH}_3)_3$ ;  $\text{CH}_3\text{CHCH}_3$  minor,  $\text{CH}_3\text{CHCH}_3$ ;  $\text{CH}_3\text{CH-ON}$ ). Yield: 41%. GPC (eluent DMF with  $\text{NH}_4\text{PF}_6$  (0.8 g/L)):  $M_n = 10,900$  g/mol, PDI = 1.15.

## 2. Techniques

Size exclusion chromatograms (SEC) were measured on a Waters SEC system consisting of an isocratic pump, a solvent degasser, a column oven, a 2996 photodiode array (PDA) detector, a 2414 refractive index detector, a 717 plus autosampler, and a Waters Styragel HT 4 GPC column (with 10  $\mu\text{m}$  particles) with a precolumn installed. The eluent was *N,N*-dimethylformamide (DMF) containing 5 mM  $\text{NH}_4\text{PF}_6$  as additive at a flow rate of 0.5 mL/min. Linear poly(ethylene glycol) with a narrow polydispersity and with a  $M_w$  range from 970 to 40 000 Da were used as standards. The column temperature was set to 323 K. Nuclear magnetic resonance spectra were recorded on a Varian Gemini 400 MHz spectrometer at 298 K.

Dynamic light scattering measurements were performed on a DynaPro<sup>TM</sup> Plate Reader<sup>TM</sup> from Wyatt Technology and a CGS-3 from Malvern apparatus equipped with a He-Ne laser with a wavelength of 632.8 nm. Micellar solutions were prepared by direct dissolution of known amounts of the bulk  $\text{PTFMS}_{20}$ -*b*-*PtBA* $_{25}$ -*b*- $\text{PS}_{35}$ - $[\text{Ru}]$ - $\text{PEG}_{70}$  sample in either ethanol or isopropanol. The temperature was varied for measurements performed with the DynaPro<sup>TM</sup> Plate Reader<sup>TM</sup> while measurements

were performed at 25 °C with the CGS-3. A quartz plate with quartz cover was used for measurements performed in the DynaPro™ Plate Reader™.

The hydrodynamic radius,  $R_h$ , of the micellar structures was determined by DLS. The experimental autocorrelation function,  $g(t)$ , is commonly expressed in the form of a cumulant expansion:

$$g(t) = \exp \left[ -\Gamma_1 t + \left( \frac{\Gamma_2}{2!} \right) t^2 - \left( \frac{\Gamma_3}{3!} \right) t^3 + \dots \right]$$

where  $\Gamma_i$  is the  $i^{\text{th}}$  cumulant, and  $\Gamma_1 = Dq^2$  where  $D$  is the translational diffusion coefficient and  $q$  is the absolute value of the scattering vector. The diffusion coefficient is related to the hydrodynamic radius  $R_h$  by the Stokes-Einstein equation:

$$R_h = \frac{k_b T}{6\pi\eta D}$$

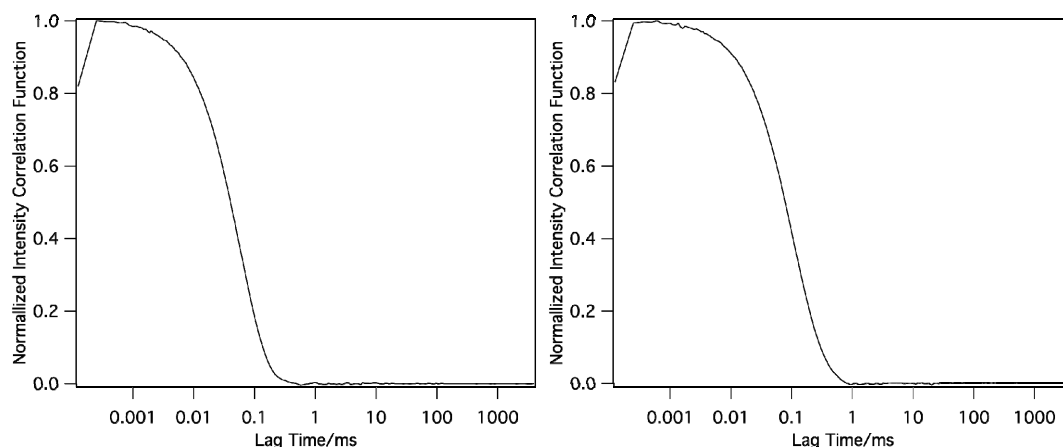
where  $k_b$  is the Boltzmann constant and  $\eta$  the viscosity of the solvent.

For DLS measurements performed with the Malvern CGS-3, data were collected at different angles and for different micellar concentrations. DLS results were analyzed by the cumulant method, while size distribution histograms were obtained by the CONTIN method. The polydispersity index (PDI) of the micelles was estimated from the  $\Gamma_2/\Gamma_1^2$  ratio in which  $\Gamma_1$  and  $\Gamma_2$  represent the first and second cumulant, respectively. No dependence of the DLS signal as a function of the angle of measurement was observed. The values obtained for  $R_h$  were extrapolated to zero concentration leading to absolute values (while only apparent values were obtained for measurements performed on the DynaPro™ Plate Reader™).

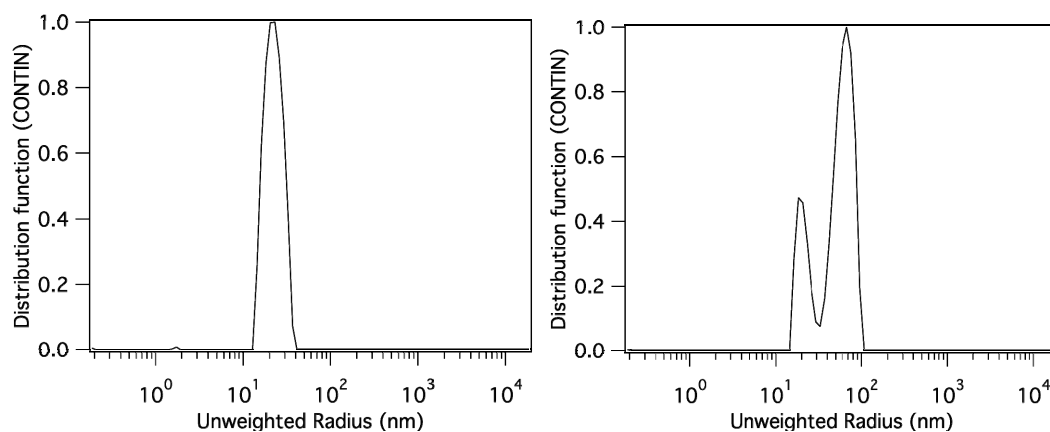
Transmission electron microscopy (TEM) measurements were performed on a FEI Tecnai 20, type Sphera TEM operating at 200 kV (LaB<sub>6</sub> filament). Images were recorded with a bottom mounted 1k × 1k Gatan CCD camera. For TEM measurements, 200 mesh carbon coated copper grids for TEM were purchased from SPI. Prior to blotting, the grids were made hydrophilic by surface plasma treatment using a Cressington 208 carbon coater operating at 5 mA for 40 s. For sample preparation a droplet of the micelle solution was blotted onto the grid and subsequently excess liquid was manually removed with filter paper. The samples were not stained.

### 3. DLS results

Typical correlation curves obtained in either ethanol or isopropanol for the PTFMS<sub>20</sub>-*b*-PtBA<sub>25</sub>-*b*-PS<sub>35</sub>-[Ru]-PEG<sub>70</sub> micelles are shown in Fig. S1 while the CONTIN histograms obtained after deconvolution of these curves are displayed in Fig. S2.



**Fig. S1.** Normalized intensity correlation functions obtained by DLS for the PTFMS<sub>20</sub>-*b*-PtBA<sub>25</sub>-*b*-PS<sub>35</sub>-[Ru]-PEG<sub>70</sub> micelles in ethanol (left) and isopropanol (right). The concentration for both solutions was 2 g/L.



**Fig. S2.** CONTIN size distribution histograms obtained by DLS for the PTFMS<sub>20</sub>-*b*-PtBA<sub>25</sub>-*b*-PS<sub>35</sub>-[Ru]-PEG<sub>70</sub> micelles in ethanol (left) and isopropanol (right). The concentration for both solutions was 2 g/L.

From the CONTIN size distribution histograms shown in Fig. S2, it is clear that the micelles formed in isopropanol are more polydisperse than the ones formed in ethanol. Indeed two populations are resolved for the micelles in isopropanol.

#### **4. Encapsulation of a fluorophilic dye in the PTFMS<sub>20</sub>-*b*-PtBA<sub>25</sub>-*b*-PS<sub>35</sub>-[Ru]-PEG<sub>70</sub> micelles in isopropanol at room temperature**

The formation of PTFMS nanodomains in the PTFMS<sub>20</sub>-*b*-PtBA<sub>25</sub>-*b*-PS<sub>35</sub>-[Ru]-PEG<sub>70</sub> micelles has been deduced from the TEM picture of those micelles shown in Fig. 3. In order to further confirm the presence of such PTFMS nanodomains, a fluorophilic dye has been synthesized and its encapsulation into the PTFMS nanodomains has been studied. The same dye as the one previously synthesized and encapsulated into fluorodomains-containing micelles by Lodge and coworkers has been used [1]. This dye, namely 1-naphthyl perfluoroheptyl ketone (NFH), should preferentially dissolve in the fluorinated PTFMS nanodomains. A 1 mg/mL micellar solution of the PTFMS<sub>20</sub>-*b*-PtBA<sub>25</sub>-*b*-PS<sub>35</sub>-[Ru]-PEG<sub>70</sub> copolymer in isopropanol was then mixed with an excess of NFH under stirring for one day. The UV-Vis adsorption spectrum of this solution was then measured and revealed the characteristic absorption of NFH molecules encapsulated in a fluorophilic domain at 298 nm, in perfect agreement with the data previously reported in [1]. In sharp contrast, this characteristic adsorption was not observed when NFH was added to a micellar solution of the PTFMS<sub>20</sub>-*b*-PtBA<sub>25</sub>-*b*-PS<sub>35</sub>-[Ru]-PEG<sub>70</sub> copolymer in ethanol. This experiment confirms the formation of PTFMS fluorophilic nanodomains for the PTFMS<sub>20</sub>-*b*-PtBA<sub>25</sub>-*b*-PS<sub>35</sub>-[Ru]-PEG<sub>70</sub> micelles in isopropanol.

[1] T. P. Lodge, A. Rasdal, Z. Li and M. A. Hillmyer, *J. Am. Chem. Soc.* 2005, **127**, 17608.