

SUPPORTING INFORMATION

for

Metallosupramolecular side-chain polymers and polyelectrolyte-metallosupramolecular surfactant complexes

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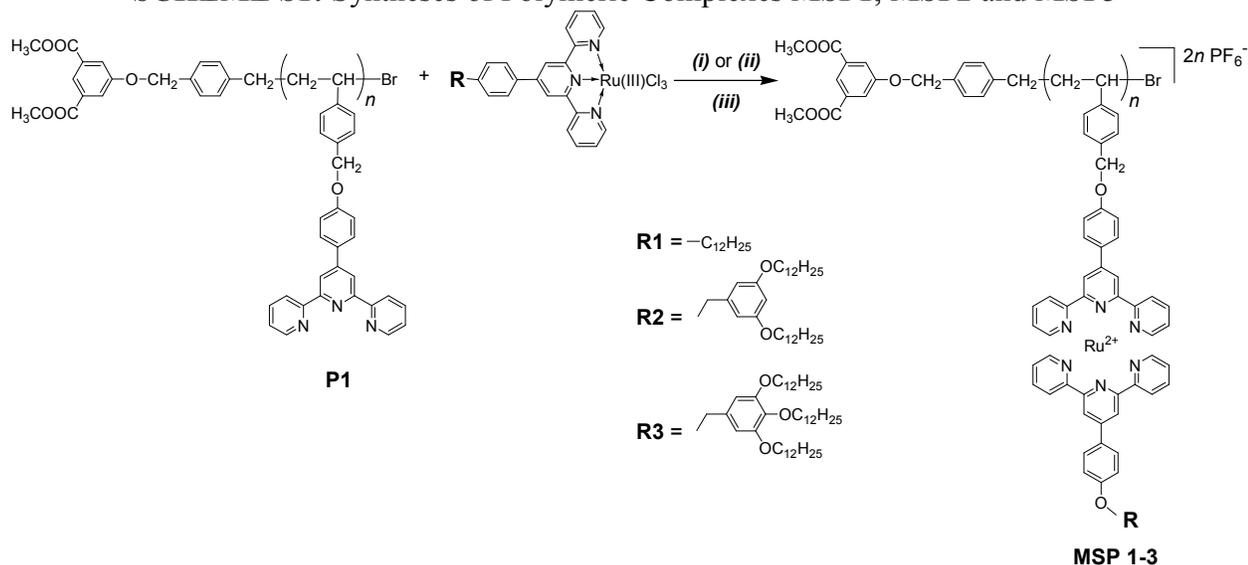
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SCHEME S1: Syntheses of Polymeric Complexes **MSP1**, **MSP2** and **MSP3**



- (i) $\text{CHCl}_3/\text{EtOH}$ 30 mL/10 mL for the **R1** and **R3**, *N*-ethylmorpholine, reflux 5d.
- (ii) THF/EtOH 30 mL/10 mL for **R2**, *N*-ethylmorpholine, reflux 5d.
- (iii) $\text{H}_2\text{O}/\text{MeOH}$ 1:10 saturated solution of NH_4PF_6 .

Polymeric Complexes **MSP1**, **MSP2**, **MSP3**

0.070 g, 0.158 mmol of polymer **P1**¹ and 0.166 g, 0.237 mmol of monocomplex **R1** or 0.235 g, 0.237 mmol of monocomplex **R2** or 0.278 g, 0.237 mmol of monocomplex **R3** were dissolved in either $\text{CHCl}_3/\text{EtOH}$ 30 mL/10 mL for the **R1**, **R3** or THF/EtOH 30 mL/10 mL for **R2**. After addition of *N*-ethylmorpholine 5 drops, the solution was degassed and refluxed for 5 days. After cooling to r.t. the mixture was filtered through Celite, which was thoroughly washed with THF and CH_3CN . The filtrate was reduced to 1/8 of its volume and to that solution was added a $\text{H}_2\text{O}/\text{MeOH}$ 1:10 saturated solution of NH_4PF_6 0.400 g (2.45 mmol). The mixture was stirred at r.t. for 24 h, filtrated and the red solid was washed repeatedly with MeOH, warm H_2O , MeOH and *n*-Hexane. After drying at high vacuum the **MSP1** polymeric complex was redissolved in THF, filtrated for the removal of any unreacted **R1**, the filtrate was rotary evaporated, redissolved in CHCl_3 and precipitated into diethyl ether. The final **MSP1** complex was obtained after drying at 45°C under high vacuum. The **MSP2** and **MSP3** polymeric complexes were obtained after redissolvance into CH_3CN , filtration to remove any unreacted **R2** or **R3**,

respectively, rotary evaporation of the filtrate, precipitation of their CHCl_3 solution into diethyl ether, and drying at 45°C under high vacuum.

Yields: **MSP1** - 90 mg (43 %), **MSP2** - 115 mg (45 %), **MSP3** - 140 mg (49 %).

MSP1: ^1H NMR ($\text{DMSO-}d_6$): 0.85 (CH_3 , s, 3H), 1.27 ($\text{CH}_2 \text{CH}_3$, m, 10H), 1.43 (CH_2 , s, 2H), 1.79 (CH_2 , s, 3H), 4.14 (OCH_2 , s, 2H), 5.30 ($\text{C}_{\text{Ar}}\text{CH}_2\text{O}$, m, 4H), 7.00-7.60 ($\text{C}_{\text{Ar}}\text{H}$, m, 16H tpy, 6H initiator), 7.94 ($\text{C}_{\text{Ar}}\text{H}$, m, 4H), 8.22 ($\text{C}_{\text{Ar}}\text{H}$, s, 1H initiator), 8.39 ($\text{C}_{\text{Ar}}\text{H}$, m, 4H), 9.06 ($\text{C}_{\text{Ar}}\text{H}$, s, 4H), 9.39 ppm ($\text{C}_{\text{Ar}}\text{H}$, s, 4H).

MSP2: ^1H NMR ($\text{DMSO-}d_6$): 0.86 (CH_3 , s, 3H), 1.27 ($\text{CH}_2 \text{CH}_3$, m, 34H), 1.43 (CH_2 , s, 4H), 1.72 (CH_2 , s, 5H), 4.00 (OCH_2 , s, 4H), 5.23 ($\text{C}_{\text{Ar}}\text{CH}_2\text{O}$, m, 6H), 6.46 ($\text{C}_{\text{Ar}}\text{H}$, s, 1H), 6.66 ($\text{C}_{\text{Ar}}\text{H}$, s, 2H), 7.00-7.50 ($\text{C}_{\text{Ar}}\text{H}$, m, 16H tpy, 6H initiator), 7.96 ($\text{C}_{\text{Ar}}\text{H}$, m, 4H), 8.2 ($\text{C}_{\text{Ar}}\text{H}$, s, 1H initiator), 8.34 ($\text{C}_{\text{Ar}}\text{H}$, m, 4H), 8.98 ($\text{C}_{\text{Ar}}\text{H}$, s, 4H), 9.29 ppm ($\text{C}_{\text{Ar}}\text{H}$, s, 4H).

MSP3: ^1H NMR ($\text{DMSO-}d_6$): 0.83 (CH_3 , s, 6H), 1.24 ($\text{CH}_2 \text{CH}_3$, m, 34H), 1.41 (CH_2 , s, 4H), 1.71 (CH_2 , s, 5H), 3.90 (OCH_2 , d, 6H), 5.17 (m, 6H), 6.77 ($\text{C}_{\text{Ar}}\text{H}$, s, 2H), 7.00-7.50 ($\text{C}_{\text{Ar}}\text{H}$, m, 16H tpy, 6H initiator), 7.91 ($\text{C}_{\text{Ar}}\text{H}$, m, 4H), 8.30 ($\text{C}_{\text{Ar}}\text{H}$, s, 1H initiator), 8.34 ($\text{C}_{\text{Ar}}\text{H}$, m, 4H), 8.96 ($\text{C}_{\text{Ar}}\text{H}$, s, 4H), 9.29 ppm ($\text{C}_{\text{Ar}}\text{H}$, s, 4H).

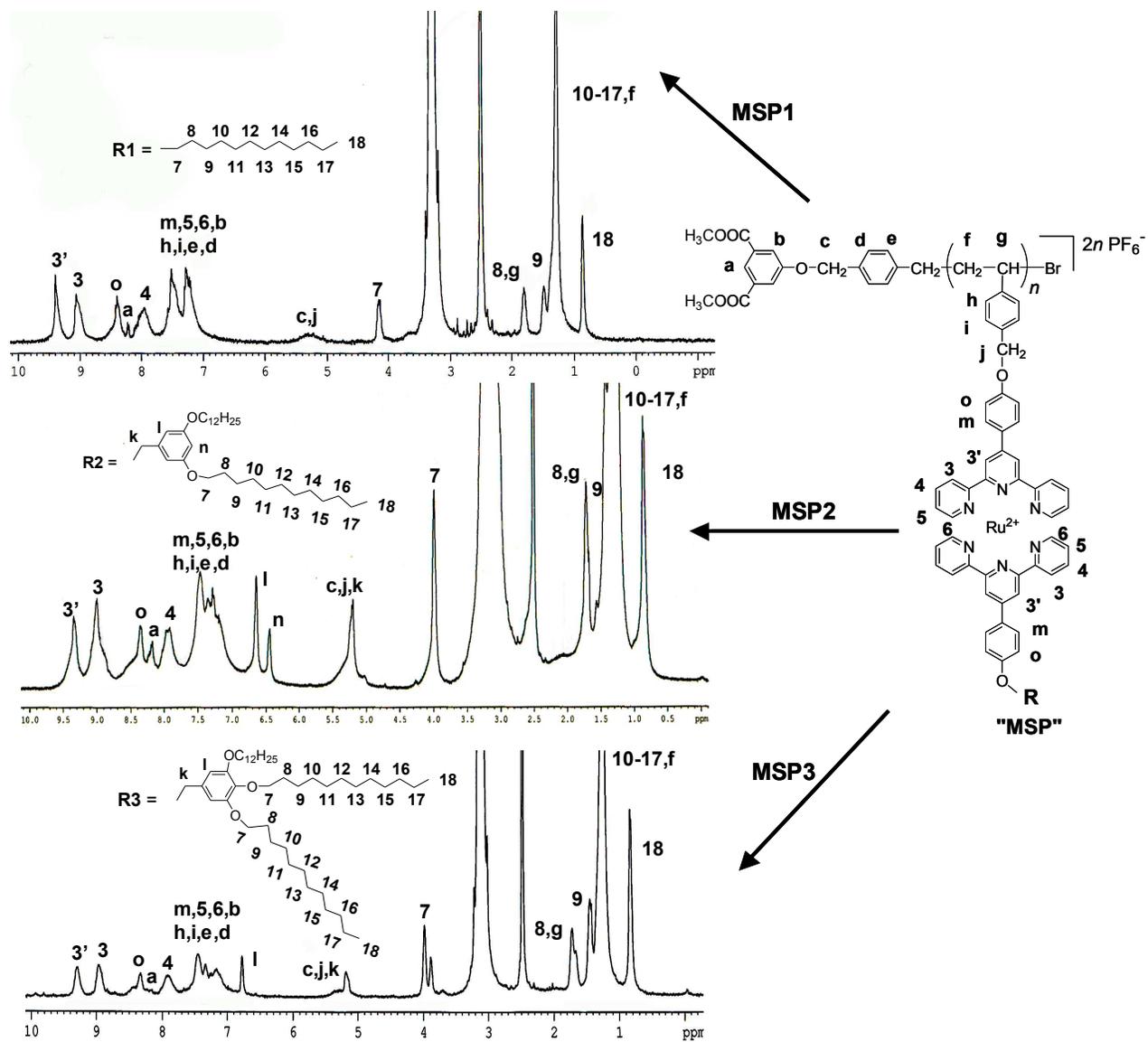
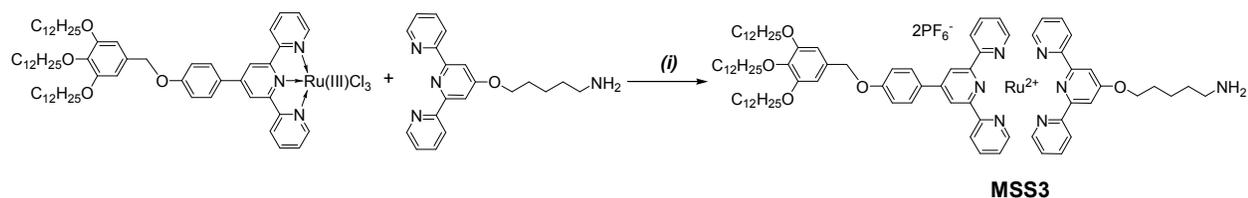


FIGURE S1: ^1H NMR of polymeric complexes MSP1, MSP2 and MSP3 in DMSO-d_6 .²

SCHEME S2: Synthesis of Complex MSS3



(i) THF/EtOH 20 mL/10 mL, *N*-ethylmorpholine, reflux 2d, H₂O/MeOH 1:10 saturated solution of NH₄PF₆

MSS3. (The synthesis of MSS1 and 2 has been recently reported.³)

The tri-dodecyloxy-terpyridine/ruthenium(III) tri-chloride monocomplex (0.33 mmol) and 5-aminopentyl 4'-(2,2':6',2''-terpyridinyl)ether⁴ (0.3 mmol) were mixed in 30 mL of a 2:1 mixture of THF/EtOH. Five drops of *N*-ethylmorpholine were added and the mixture was heated to reflux for 2 days. After removing insoluble byproducts by filtration through celite, the resulting deep red filtrate was evaporated to almost half its volume. Addition of excess of a saturated NH₄PF₆/MeOH/H₂O solution caused the complex to precipitate as a red powder, which was filtrated and washed with EtOH, H₂O, EtOH, *n*-hexane and diethyl ether.

MSS3:Yield 75% δ_{H} (400 MHz; DMSO-d₆; Me₄Si): 9.42 (s, 2H, ArH), 9.08 (d, 2H, ArH), 8.88 (s, 2H, ArH), 8.78 (d, 2H, ArH), 8.42 (d, 2H, ArH), 8.02 (m, 4H, ArH), 7.20-7.48 (m, 10H, ArH), 6.8 (s, 2H, ArH), 5.21 (s, 2H, ArCH₂O), 4.59 (t, 2H, CH₂), 3.99 (t, 4H, OCH₂), 3.86 (t, 2H, OCH₂), 2.90 (m, 2H, CH₂), 2.00 (m, 4H, CH₂, NH₂), 1.73-1.65 (m, 6H, CH₂), 1.1-1.45 (m, 54H, CH₂), 0.84 (t, 9H, CH₃).

PAA(MSS) complexes. Poly(acrylic acid) (Weight-average molecular mass = 2000 Da) was purchased from Aldrich. Water was obtained from a Milli-Q purification system and had conductivity of 18 M Ω /cm. To a 10 mg/mL solution of the given MSS (**1**, **2**, or **3**) in acetone was added 1 equivalent of HCl (0.5M) in order to form the ammonium chloride. This solution was then diluted with 19 parts of water to reach a final concentration of 0.5 mg/mL and the pH adjusted back up to 6 with a small amount of NaOH. Such solutions of charged MSS**1** and MSS**2** showed no precipitation over a matter of weeks. For solutions of MSS**3**, this was not the case; small amounts of precipitate could be perceived after a few days. Complexes were obtained by drop-wise addition of charged MSS solution to a vigorously stirred solution of charged PAA (0.5 mg/mL in water, adjusted with NaOH to pH = 6.4) in a molar ratio of 1:1 (surfactants to AA repeat units). The charge-neutral complex precipitated easily, and after 30 additional minutes of stirring, the complex was collected by centrifugation, washed with water (pH ~6), and dried in a vacuum oven at 50 °C overnight.

Sample preparation for scattering experiments. All MSP and PAA(MSS) samples were cast from chloroform solution, with the solvent being allowed to evaporate slowly at room temperature and pressure. They were then annealed in saturated chloroform vapor at room temperature for a further 24h. Finally, residual traces of solvent were removed in vacuum.

Small- and wide-angle X-ray scattering. X-ray scattering diffractograms in the range of $0.08 \text{ nm}^{-1} < q < 25 \text{ nm}^{-1}$ were recorded using an Anton-Parr SAXSess system. The system uses a sealed tube Cu K α ($\lambda = 1.542 \text{ \AA}$) source and is operated with a Kratky block camera and a line-collimated primary beam. The scattering pattern is recorded on an image plate located 26.33 cm behind the sample.

Polarizing Optical Microscopy. A small amount of a concentrated solution (>20% by weight) of a given MSP in chloroform was placed onto a glass slide and sheared/spread onto the slide with a glass cover slip. The cover slip was then removed and the MSP sample was allowed to dry. Samples were then observed between crossed polarizers under 16x magnification.

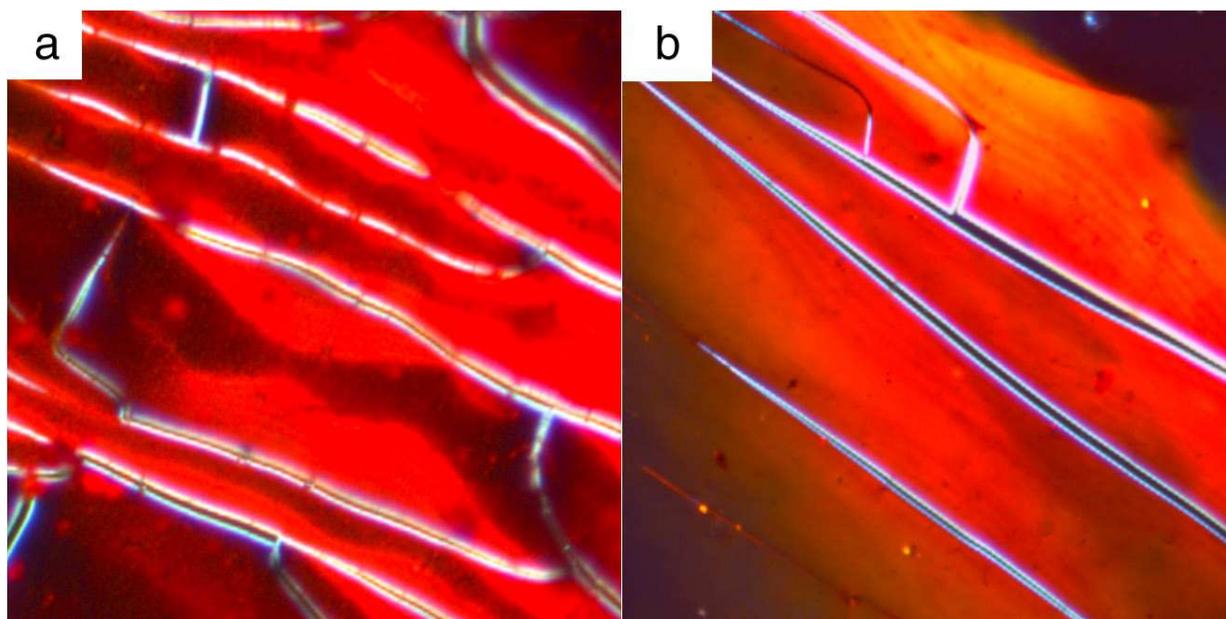


FIGURE S2: CPOM images of **MSP1** (a) and **MSP3** (b) samples prepared by the shearing procedure. Image full width is 500 microns.

References and Notes

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