This journal is © The Royal Society of Chemistry 2014

Electronic Supplementory Information

Light-Harvesting of Polymerizable 4-Hydroxy Thiazole Monomers by Energy Transfer Toward Photoactive Os(II) Metal Complexes in Linear Polymers

Alexander M. Breul,[1,2] Inês Rabelo de Moares,[2,3,4] Roberto Menzel,[1,2] Michael Pfeffer,[6] Andreas Winter,[1,2] Martin D. Hager,[1,2] Sven Rau,[6] Benjamin Dietzek,[2,3,4] Rainer Beckert,[1,2]* Ulrich S. Schubert[1,2,5]*

[1] Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstr. 10, 07743 Jena, Germany

[2] Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Philosophenweg 7, 07743 Jena, Germany

[3] Leibnitz Institute of Photonic Technology (IPHT), Albert-Einstein-Straße 9, 07745 Jena, Germany

[4] Institute of Physical Chemistry (IPC) and Abbe Center of Photonics, Friedrich Schiller University Jena, Helmholtzweg 4, 07743 Jena, Germany

[5] Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, The Netherlands

[6] Institute of Inorganic Chemistry I, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany

*Author for correspondence:

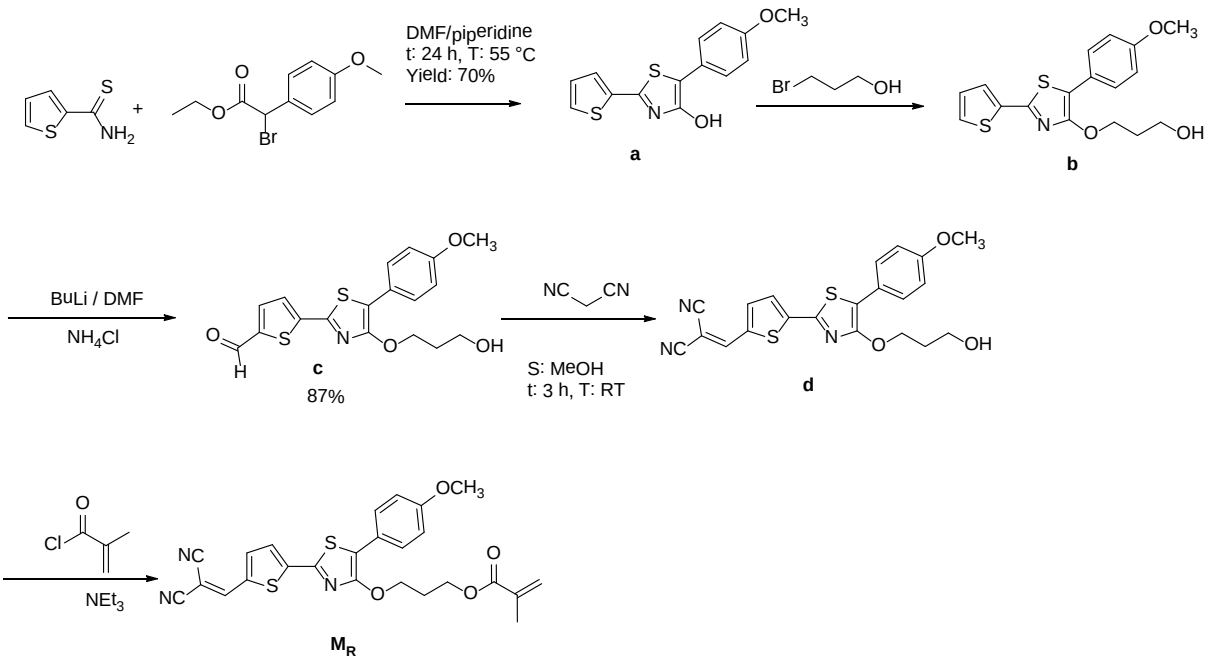
Prof. Dr. U. S. Schubert. Telephone: +49 (0)3641 948200, Fax: +49 (0)3641 948202,

E-mail: ulrich.schubert@uni-jena.de, Internet: www.schubert-group.com

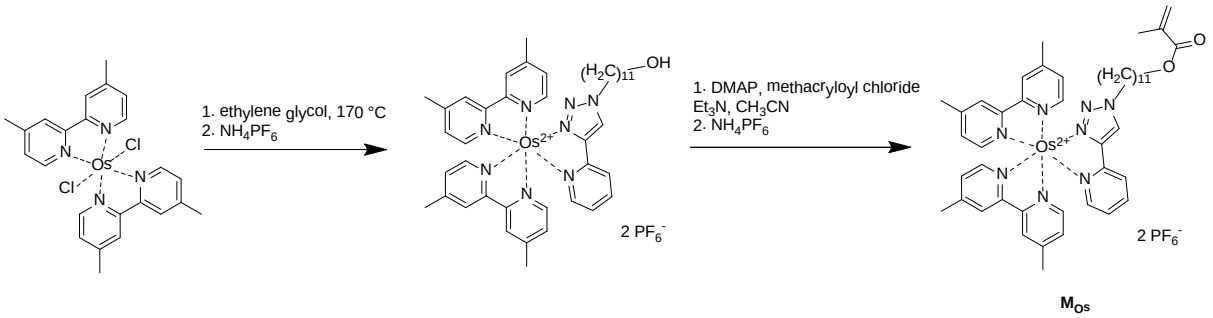
Prof. Dr. R. Beckert. Telephone: +49 (0)3641 948230, Fax: +49 (0)3641 948212,

E-mail: rainer.beckert@uni-jena.de, Internet: http://www.agbeckert.uni-jena.de/

This journal is © The Royal Society of Chemistry 2014



Scheme 1. Schematic representation of the synthesis of $\mathbf{M_R}$.



Scheme 2. Schematic representation of the synthesis of $\mathbf{M_{Os}}$.

Experimental

5-(4-Methoxyphenyl)-2-(thiophen-2-yl)thiazol-4-ol (**a**)

Synthesis according to a literature procedure[1]: To a solution of 3.25 g (22.7 mmol) thiophene-2-carbothioamide in 50 mL DMF were added 9.30 g (34.1 mmol, 1.5 eq.) ethyl 2-bromo-2-(4-methoxyphenyl)acetate and 2.00 g (23.5 mmol) piperidine. The red solution was heated to 50 °C and maintained there for 24 h under permanent stirring. After cooling down to RT, H_2O (100 mL) was added and the product precipitated as a yellow solid. The mixture was

stirred for additional 30 min. The product was filtered off, washed thoroughly with EtOH and diethyl ether and dried *in vacuo*. The light yellow solid can be used without further purification. Yield: 4.6 g (15.9 mmol), 70%. **^{1}H NMR (250 MHz, DMSO-*d*$_6$)**: δ = 3.75 (s, 3H), 6.96 (d, *J* = 8.77 Hz, 2H), 7.15 (dd, *J* = 4.73 Hz, *J* = 3.98 Hz, 1H), 7.65-7.54 (m, 3H), 7.68 (d, *J* = 4.93 Hz, 1H), 11.41 (s, 1H). **^{13}C NMR (63 MHz, DMSO-*d*$_6$)**: δ = 157.56, 156.64, 152.51, 136.71, 128.46, 128.33, 127.12, 125.98, 123.96, 114.23, 106.58, 55.05. **MS (EI)**: 289 ($M^{\cdot+}$, 100%), 274 ($M^{\cdot+}$ - CH_3, 15%). **EA for $C_{14}H_{11}NO_2S_2$**: C 58.11, H 3.83, N 4.84, S 22.16; found: C 58.27, H 4.08, N 4.47, S 21.80. **mp**: 227-228 °C.

3-(5-(4-Methoxyphenyl)-2-(thiophen-2-yl)thiazol-4-yloxy)propan-1-ol (**b**)

To a solution of **a** (1.50 g, 5.19 mmol) and 3-bromopropane-1-ol (1.08 g, 7.79 mmol, 1.5 eq.) in DMSO (50 mL) was added fine ground K_2CO_3.(0.86 g, 6.22 mmol, 1.2 eq.). The red mixture was stirred for 24 h at room temperature followed by the addition of H_2O (200 mL). The product was extracted with $CHCl_3$ (2 × 100 mL). The combined organic phases were washed additionally with H_2O (3 × 100 mL) to remove the DMSO, dried over $MgSO_4$ and concentrated *in vacuo*. The brown oil was purified by applying a short gel filtration (silica, $CHCl_3$:EtOAc 4:1) to yield the pure ether as a yellow oil which solidifies after a few hours. The product can also be recrystallized from *n*-heptane/CH_2Cl_2 by slowly evaporation of the CH_2Cl_2 and adding of a seed crystal. Yield: 1.29 g (3.71 mmol), 72%. **^{1}H NMR (250 MHz, $CDCl_3$)**: δ = 7.60 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 3.6 Hz, 1H), 7.34 (d, *J* = 5.0 Hz, 1H), 7.04 (dd, *J* = 5.0 Hz, 3.7 Hz, 1H), 6.89 (s, *J* = 8.8 Hz, 2H), 4.61 (t, *J* = 5.8 Hz, 2H), 3.83 (m, 5H), 3.15 (s, 1H), 2.03 (p, *J* = 5.8 Hz, 2H). **^{13}C NMR (63 MHz, $CDCl_3$)**: δ = 158.55, 157.60, 153.74, 137.54, 128.19, 128.09, 127.43, 125.67, 123.89, 114.30, 111.17, 67.94, 67.85, 59.06, 55.40, 33.05. **MS (EI)**: 347 [$M^{\cdot+}$] (100), 289 (80), 151 (90). **EA for $C_{17}H_{17}NO_3S_2$**: C 58.77, H 4.93, N 4.03, S 18.46; found: C 58.61, H 4.72, N 3.92, S 18.27.

5-(4-(3-Hydroxypropoxy)-5-(4-methoxyphenyl)thiazol-2-yl)thiophene-2-carbaldehyde (**c**)

To a solution of **b** (2.80 g, 8.06 mmol) in dry THF (50 mL) was slowly added *n*-BuLi (6.77 mL, 16.9 mmol, 2.1 equiv., 2.5 M in hexanes) at –78 °C under a nitrogen atmosphere. The mixture was stirred for 30 min. After warming to room temperature and additional stirring for 30 min, the mixture was cooled again to –78 °C and dry DMF (2 mL) was added and stirring was continued for 30 min followed by warming up to room temperature and additional stirring for 1 h. The mixture was neutralized with saturated NH_4Cl solution, diluted with $CHCl_3$ (100 mL) and washed with H_2O (3 × 100 mL). The organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatography (silica, EtOAc:heptane 1:1 to 1:0) yielded the product as an orange solid. If small amounts of optical impurities are present, the compound can be efficiently recrystallized from a mixture of CH_2Cl_2/heptane by slowly evaporation of the CH_2Cl_2. Yield: 2.63 g (7.00 mmol), 87%. **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 9.89 (s, 1H), 7.69 (d, J = 4.0 Hz, 1H), 7.67-7.58 (m, 2H), 7.47 (d, J = 4.0 Hz, 1H), 6.99-6.87 (m, 2H), 4.63 (t, J = 5.9 Hz, 2H), 3.93-3.77 (m, 5H), 2.35 (t, J = 5.9 Hz, 1H), 2.08 (p, J = 5.9 Hz, 2H). **^{13}C NMR (63 MHz, $CDCl_3$)**: δ = 182.79, 159.11, 158.42, 151.27, 146.22, 143.65, 136.74, 128.49, 125.46, 123.41, 114.49, 114.40, 68.22, 59.62, 55.50, 32.84. **MS (Micro-ESI)**: 398.1 [M + Na^+]. **EA for $C_{18}H_{17}NO_4S_2$**: C, 57.58; H, 4.56; N, 3.73; S, 17.08. Found: C, 57.61; H, 4.55; N, 3.65; S, 16.94. **UV/Vis (CH_3CN): λ_{max} (log ε)**: 234 (4.00), 273 (3.95), 433 (4.32).

2-((5-(4-(3-Hydroxypropoxy)-5-(4-methoxyphenyl)thiazol-2-yl)thiophen-2-yl)methylene)malononitrile (**d**)

To a solution of **c** (800 mg, 2.13 mmol) and malononitrile (155 mg, 2.34 mmol, 1.1 equiv.) in MeOH (30 mL) at RT was added one drop of pyridine. The orange solution turned deep red

and was stirred till no educt was left (TLC). The mixture was concentrated (avoid heat!) *in vacuo*. Purification was achieved either by gel filtration (silica, EtOAc:heptane 1:1) or recrystallization by slowly diffusion from pentane in an acetone solution of the nitrile yielding the product as a deep purple crystalline compound. Yield: 820 mg (1.94 mmol), 91%. **^{1}H NMR (250 MHz, $CDCl_3$):** δ = 7.73 (s, 1H), 7.68 (d, J = 4.3 Hz, 1H), 7.66-7.60 (m, 2H), 7.47 (d, J = 4.2 Hz, 1H), 7.00-6.88 (m, 2H), 4.64 (t, J = 6.0 Hz, 2H), 3.92-3.76 (m, 5H), 2.20-2.04 (m, 3H). **^{13}C NMR (63 MHz, $CDCl_3$)**: δ = 159.38, 158.97, 150.06, 149.80, 148.00, 139.26, 135.45, 128.58, 125.68, 123.19, 115.89, 114.59, 114.14, 113.30, 68.46, 59.79, 55.52, 32.72. **MS (EI)**: 423.5 [M^+] (100), 365 (80%), 186 (50).

3-(2-(5-(2,2-Dicyanovinyl)thiophen-2-yl)-5-(4-methoxyphenyl)thiazol-4-yloxy)propyl methacrylate (**M_R**)

To a solution of **d** (430 mg, 1.02 mmol) and TEA (205 mg, 2.03 mmol, 2 equiv.) in dry CH_2Cl_2 (10 mL) was added methacryloyl chloride (127 mg, 1.22 mmol, 1.2 equiv). The reaction was stirred in a brown two necked flask under a nitrogen atmosphere at RT and was monitored by TLC. After the reaction was finished (typically after 24 h), the organic phase was washed thoroughly with saturated $NaHCO_3$ solution and H_2O (3 × 20 mL), dried over $MgSO_4$ and evaporated to dryness at T < 40 °C giving rise to a red solid. The crude product was purified using column chromatography (silica, $CHCl_3$:EtOAc 10:1) affording the methacrylate as a red crystalline compound. Yield: 401 mg (0.82 mmol), 80%. **^{1}H NMR (400 MHz, DMSO-d_6):** δ = 8.63 (s, J = 4.4 Hz, 1H), 7.89 (d, J = 4.2 Hz, 1H), 7.77 (d, J = 4.1 Hz, 1H), 7.62 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.9 Hz, 2H), 6.03 (s, 1H), 5.64 (s, J = 1.5 Hz, 1H), 4.52 (t, J = 6.2 Hz, 2H), 4.28 (t, J = 6.3 Hz, 2H), 3.79 (s, 3H), 2.16 (p, J = 6.3 Hz, 2H), 1.86 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)**: δ = 166.47, 158.78, 157.86, 152.28, 149.87, 145.89, 141.66, 135.77, 135.57, 128.07, 126.79, 125.71, 122.41, 114.79, 114.52, 114.34,

113.65, 76.04, 67.52, 61.29, 55.20, 28.26, 17.91. **MS (EI)**: 492 [M^+] (20), 365 (10), 153 (100). **UV/Vis (CH_3CN): λ_{max} (log ε)**: 497 (4.55), 344 (3.94). Φ_{Em} = 13% (CH_3CN) and 23% (MeOH) relative to Texas Red

[(dm-bpy)$_2$Os^{II}(HO-C$_{11}$H$_{22}$-trz-py)](PF$_6$)$_2$

A suspension of [Os(dm-bpy)$_2$Cl$_2$] (519 mg, 0.794 mmol) and the HO-$C_{11}H_{22}$-2-(1*H*-1,2,3-triazol-4-yl)-pyridine (261 mg, 0.825 mmol) in ethylene glycol (20 mL) was degassed with nitrogen for 1 hour. Subsequently, a catalytic amount of *N*-ethylmorpholine was added as reducing agent. This mixture was heated under microwave irradiation (170 °C) for 10 hours. After dilution with water and filtration an excess of NH_4PF_6 (~250 mg) was added to precipitate the crude product. Final purification was achieved by column chromatography (silica gel, CH_3CN/H_2O/sat. aq. KNO_3 100:10:1). The combined fractions were dissolved in an ethanol/acetonitrile mixture, filtrated and an excess of NH_4PF_6 (250 mg) was added to precipitate the product. Intensive washing with water yielded the desired complex as black oil (220 mg, 0.189 mmol, 24%). **^{1}H NMR (300 MHz, CD_3CN)** δ (ppm) = 8.65 (4H, dm-bpy, Ar-H$^{3,3'}$), 8.33 (4H, dm-bpy, Ar-H$^{6,6'}$), 8.27 (1H, trz-py-H), 8.09 (1H, trz-py-H), 7.80 (1H, trz-py-H), 7.54 (1H, trz-H), 7.18 (4H, dm-bpy, Ar-H$^{5,5'}$), 7.11 (1H, trz-py-H), 4.32 (2H, trz-CH_2), 3.48 (2H, CH_2-OH), 2.62 (12H, CH_3-py), 2.50-0.95 (18H, alkyl-CH_2). **ESI-TOF MS:** *m/z* = 438.1908 ([M-2PF_6]$^{2+}$), 1021.3550 ([M-PF_6]$^+$). **HR-ESI-TOF MS:** calcd. for [$C_{42}H_{52}N_8OOs$]$^{2+}$: *m/z* = 438.1935, found: 438.1946.

[(dm-bpy)$_2$Os^{II}(MA-C$_{11}$H$_{22}$-trz-py)](PF$_6$)$_2$ (**M$_{Os}$**)

The esterification reaction was carried out using analogous reaction conditions as previously described.[2] In this case, 220 mg (0.189 mmol) of [(dm-bpy)$_2$Os^{II}(HO-$C_{11}H_{22}$-trz-py)](PF$_6$)$_2$ were used. Yield: 78%, black oil. **^{1}H NMR (250 MHz, CD_3CN):** δ (ppm) = 8.65 (4H, dm-bpy, Ar-H$^{3,3'}$), 8.33 (4H, dm-bpy, Ar-H$^{6,6'}$), 8.27 (1H, trz-py-H), 8.10 (1H, trz-py-H), 7.80

(1H, trz-py-H), 7.54 (1H, trz-H), 7.48 (1H, trz-H), 7.18 (4H, dm-bpy, Ar-$H^{5,5'}$), 7.09 (1H, trz-py-H), 6.03 (1H, vinyl-MA), 5.45 (1H, vinyl-MA), 4.31 (2H, trz-CH_2), 4.11 (2H, CH_2-MA), 2.61 (12H, CH_3-py), 2.5-1.8 (21H, alkyl-CH_2, MA-CH_3). **MALDI-TOF MS (dithranol):** *m/z* = 1089.638 ($[M-PF_6]^+$), 944.6520 ($[M-2PF_6]^+$). **HR-ESI-TOF MS:** calcd. for $[C_{46}H_{56}N_8O_2Os]^{2+}$: 472.2066, found: 472.2065.

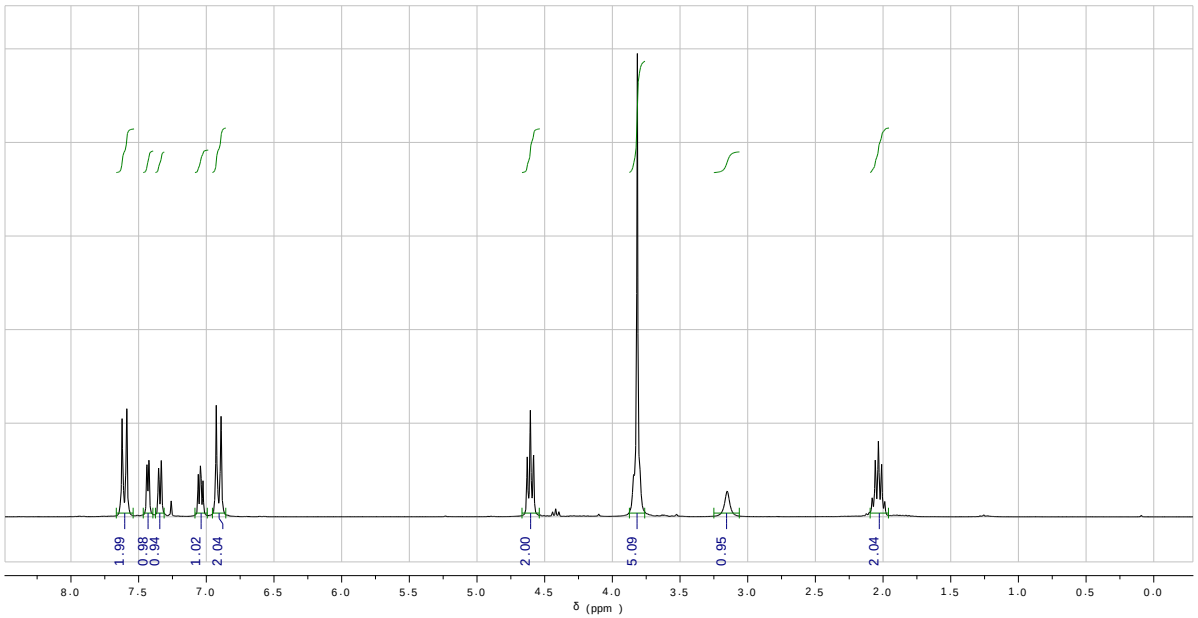


Figure 1. ^{1}H NMR (250 MHz, $CDCl_3$) of **b**.

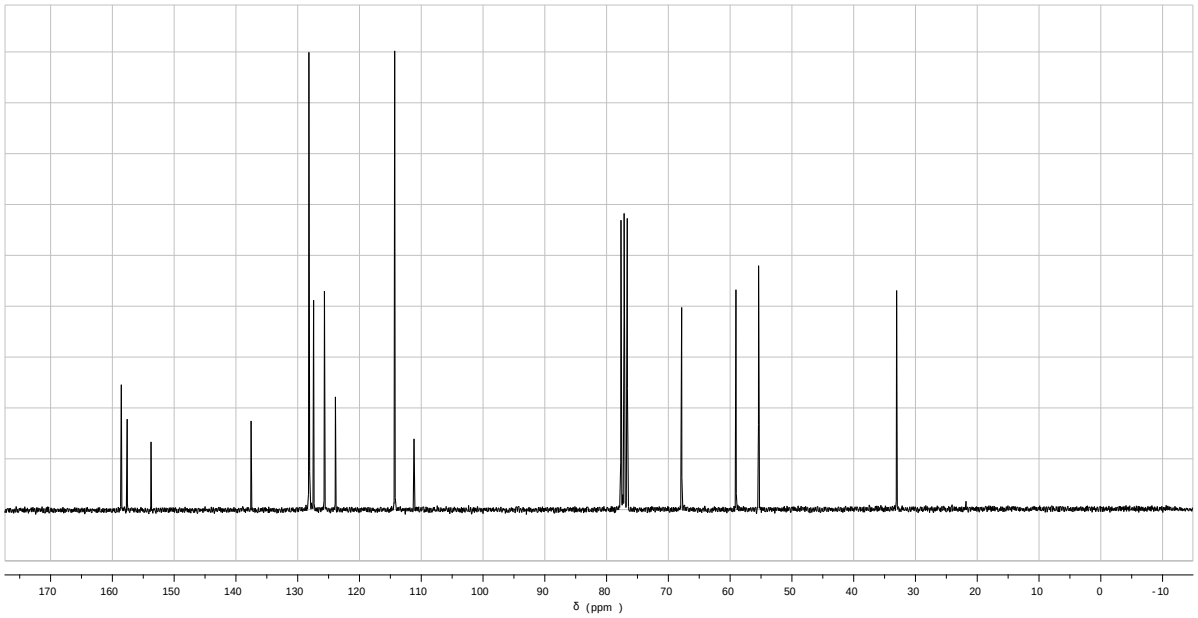


Figure 2. ^{13}C NMR (63 MHz, $CDCl_3$) of **b**.

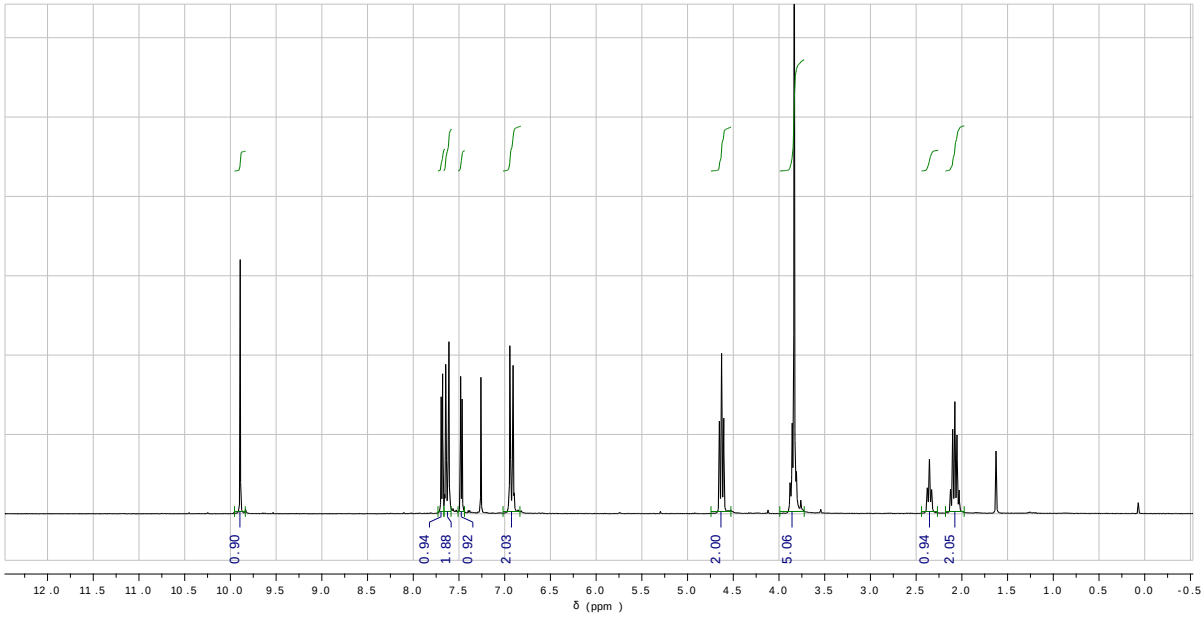


Figure 3. ^{1}H NMR (250 MHz, $CDCl_3$) of **c**.

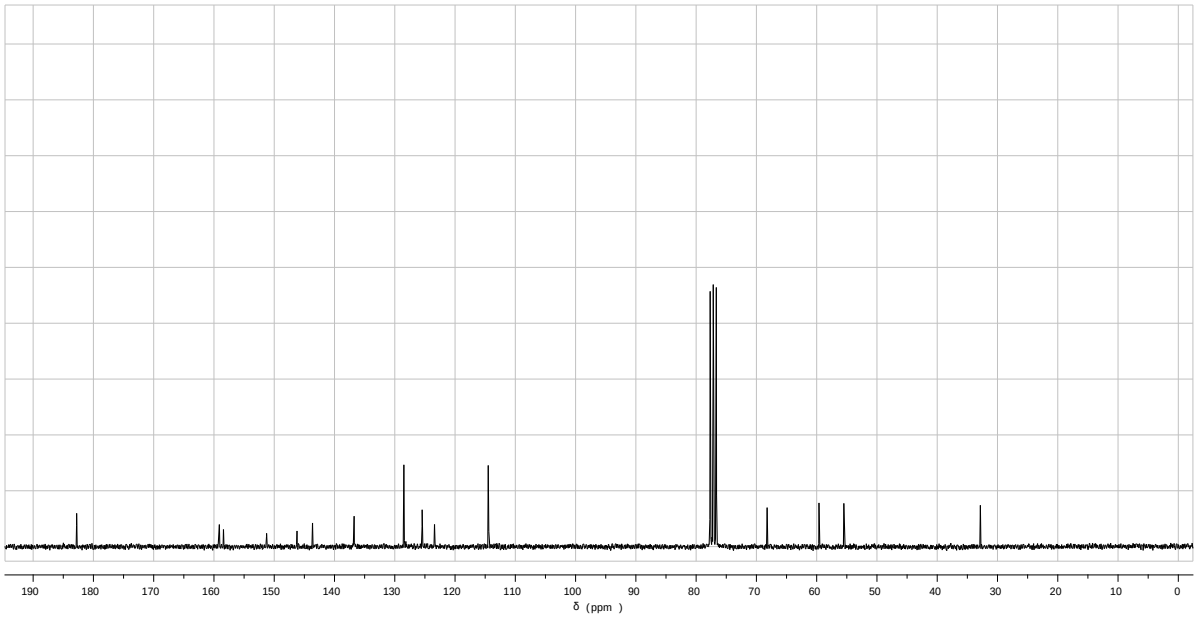


Figure 4. ^{13}C NMR (63 MHz, $CDCl_3$) of **c**.

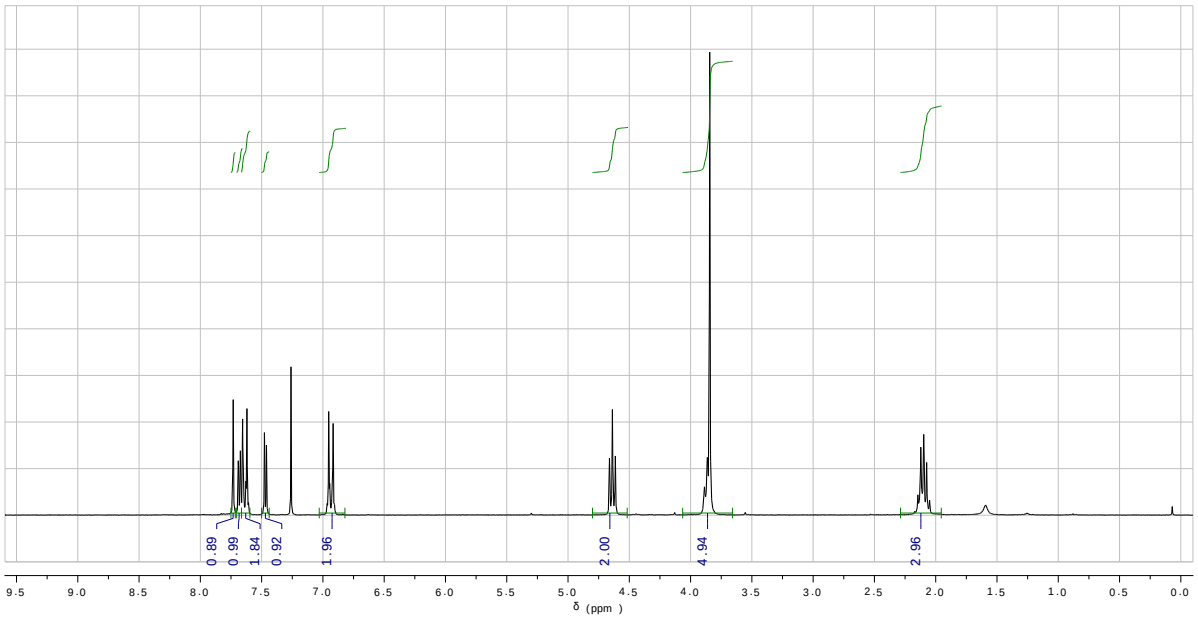


Figure 5. ^{1}H NMR (250 MHz, $CDCl_3$) of **d**.

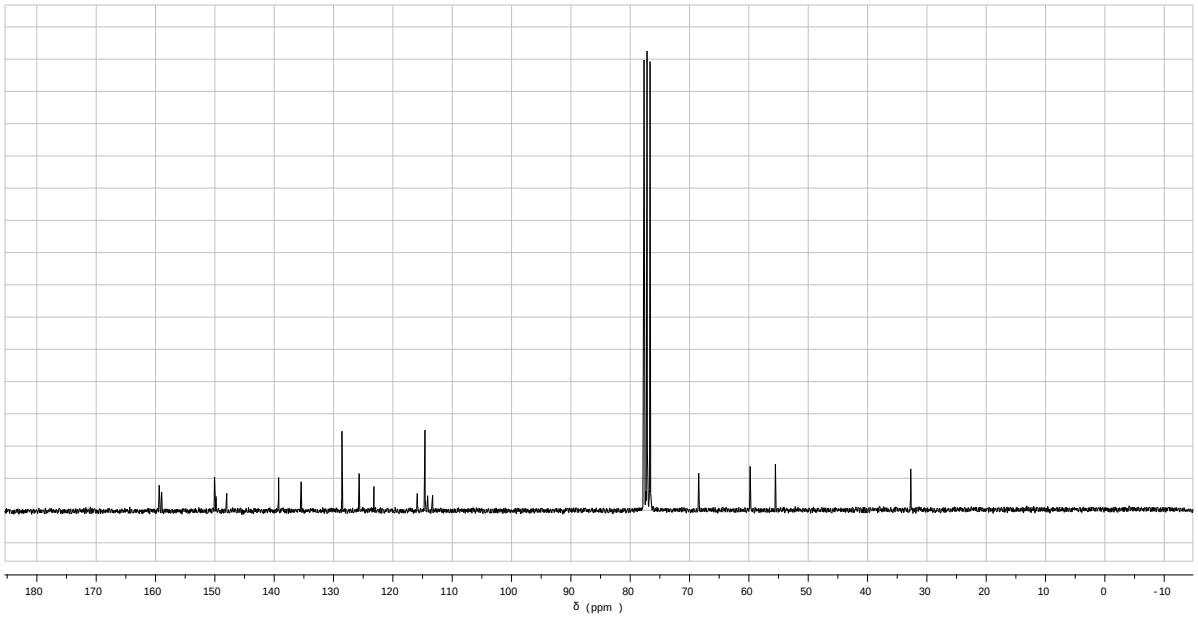


Figure 6. ^{13}C NMR (63 MHz, $CDCl_3$) of **d**.

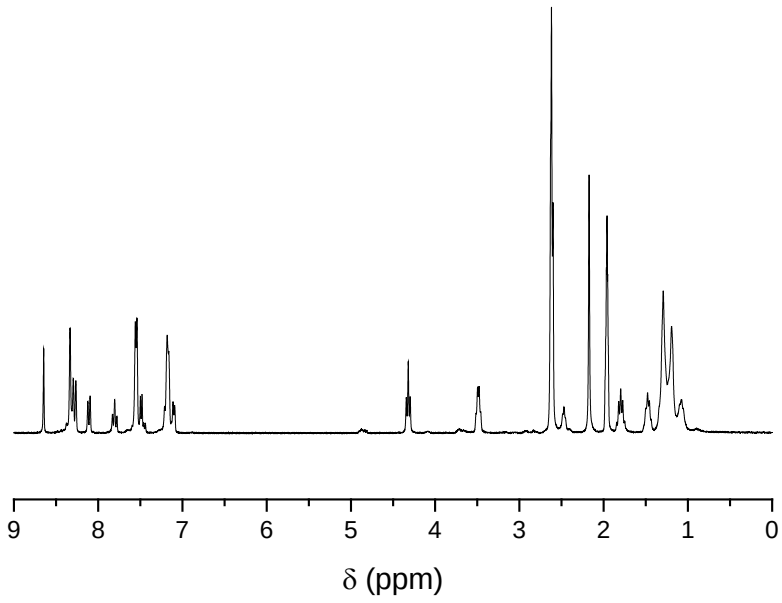


Figure 7. ^{1}H NMR (300 MHz, CD_3CN) of $[(dm\text{-}bpy)_2Os^{II}(HO\text{-}C_{11}H_{22}\text{-}trz\text{-}py)](PF_6)_2$.

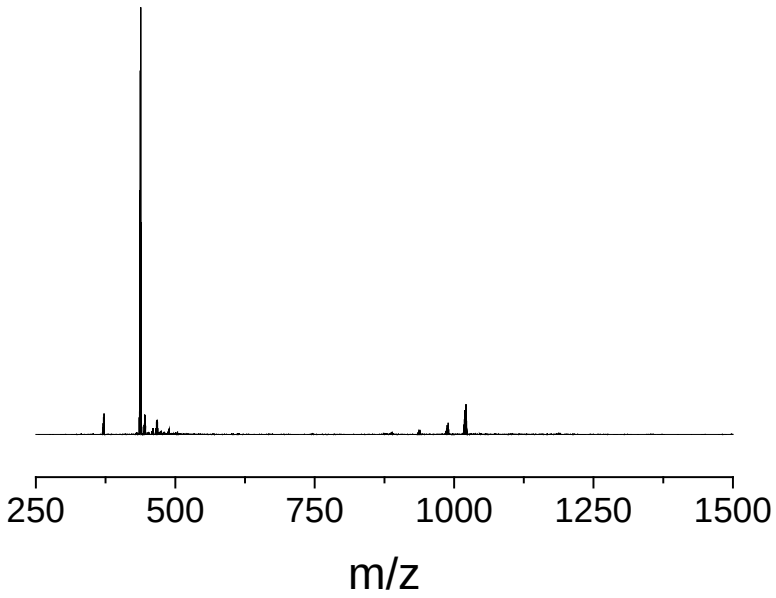


Figure 8. ESI-TOF MS of $[(dm\text{-}bpy)_2Os^{II}(HO\text{-}C_{11}H_{22}\text{-}trz\text{-}py)](PF_6)_2$.

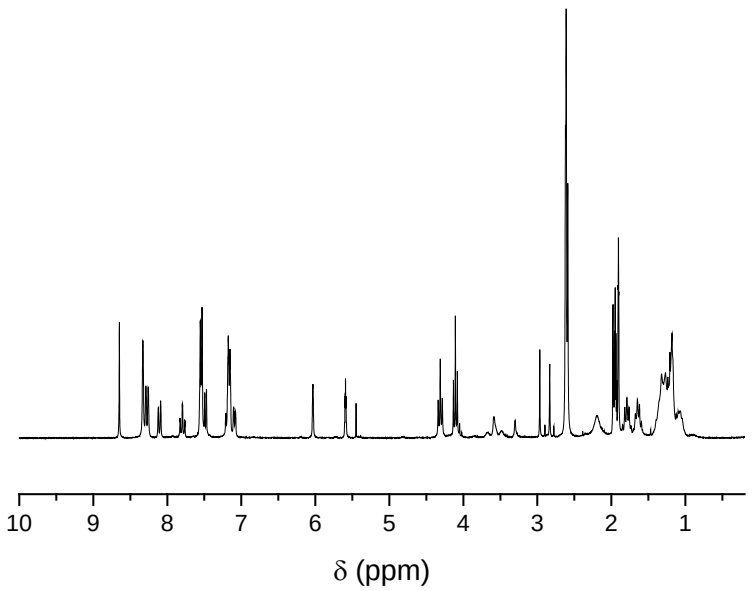


Figure 9. ^1H NMR (250 MHz. CD_3CN) of $[(dm\text{-}bpy)_2Os^{II}(MA\text{-}C_{11}H_{22}\text{-}trz\text{-}py)](PF_6)_2$.

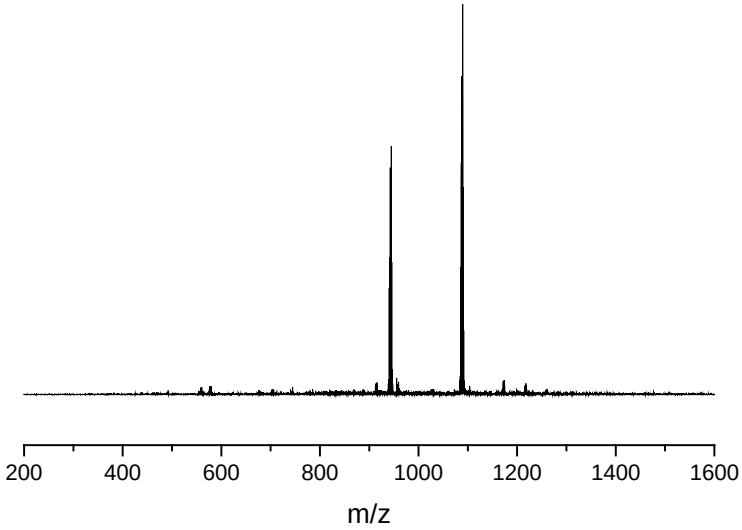


Figure 10. MALDI-TOF MS (matrix: dithranol) of $[(dm\text{-}bpy)_2Os^{II}(MA\text{-}C_{11}H_{22}\text{-}trz\text{-}py)](PF_6)_2$.

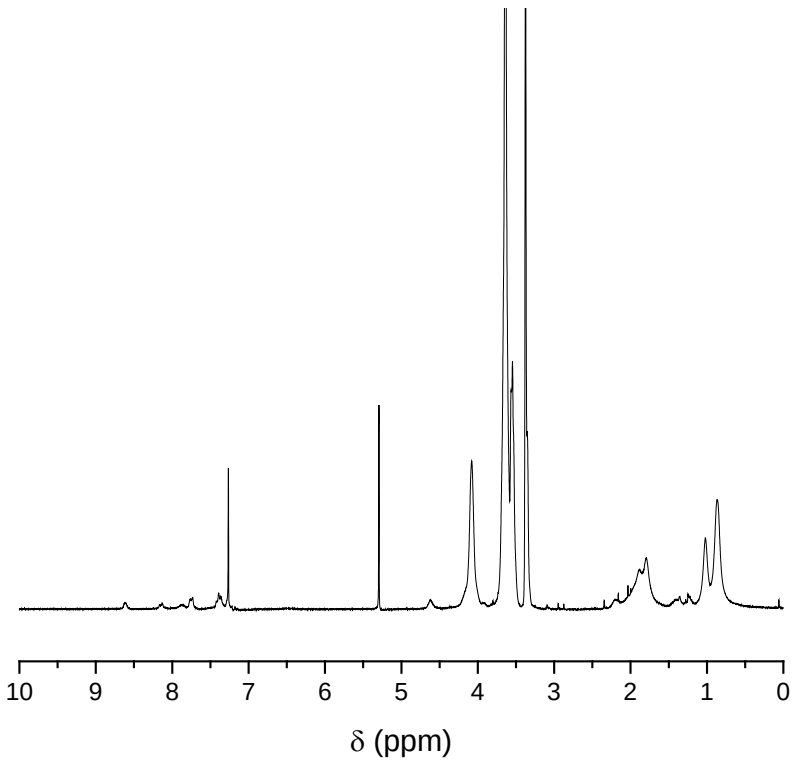


Figure 11. ^1H NMR (250 MHz, CD_2Cl_2) of $\mathbf{P_B}$.

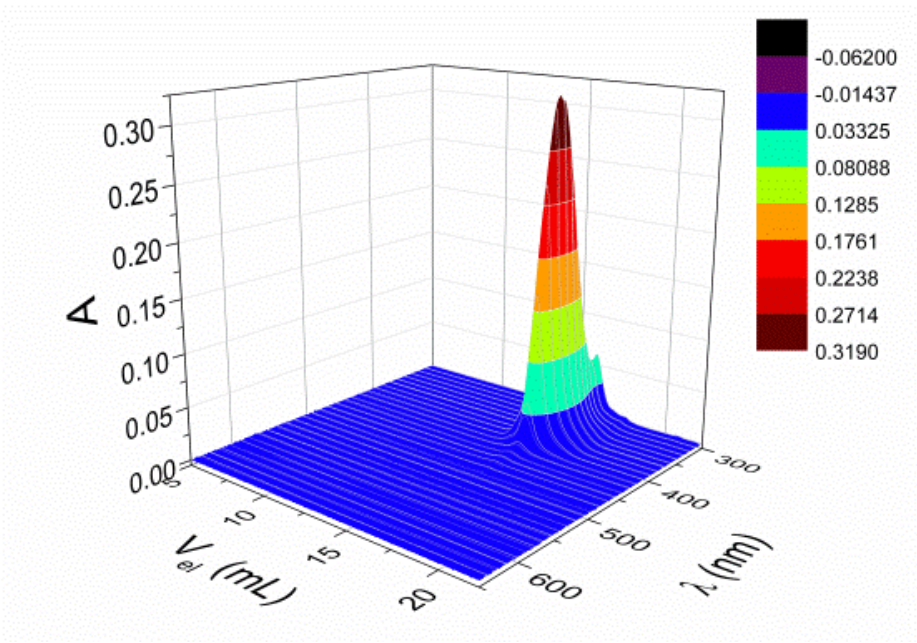


Figure 12. 2D-SEC (DMA, NH_4PF_6, PDA detector) of $\mathbf{P_B}$.

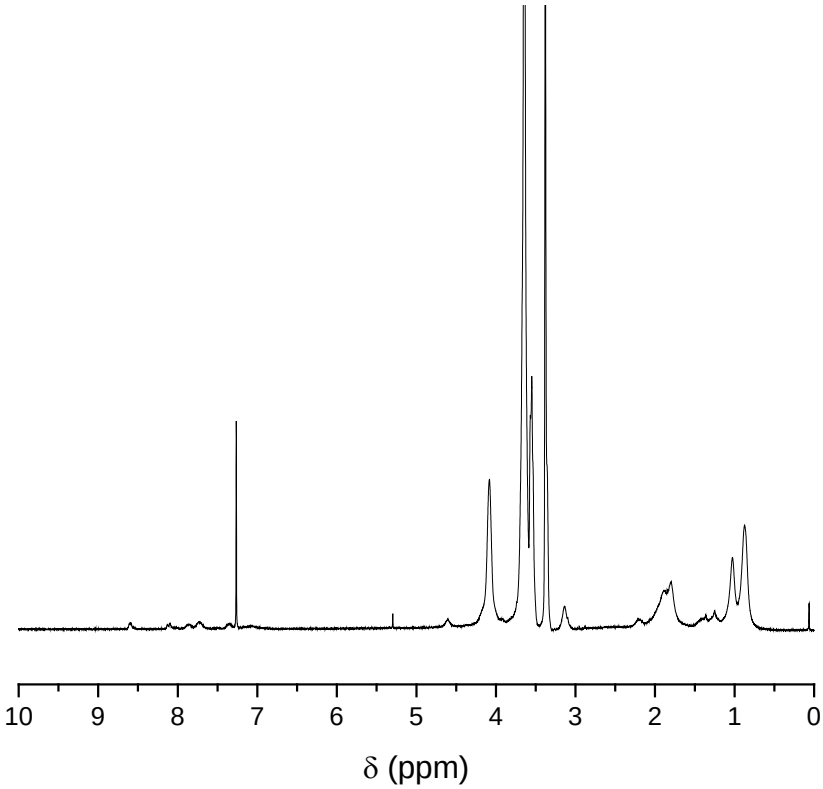


Figure 13. ^{1}H NMR (250 MHz, $CDCl_3$) of $\mathbf{P_Y}$.

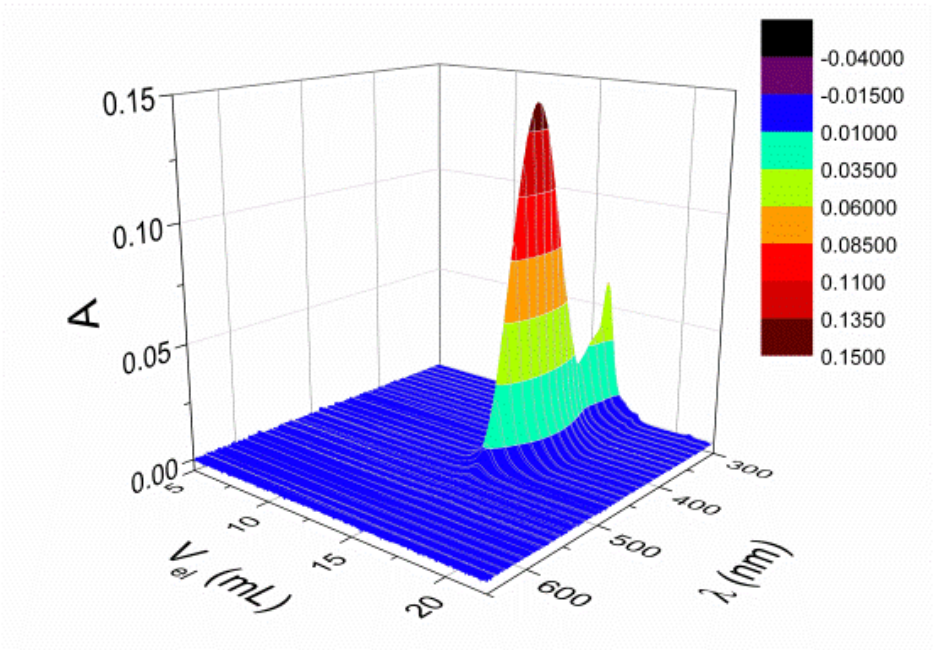


Figure 14. 2D-SEC (DMA, NH_4PF_6, PDA detector) of $\mathbf{P_Y}$.

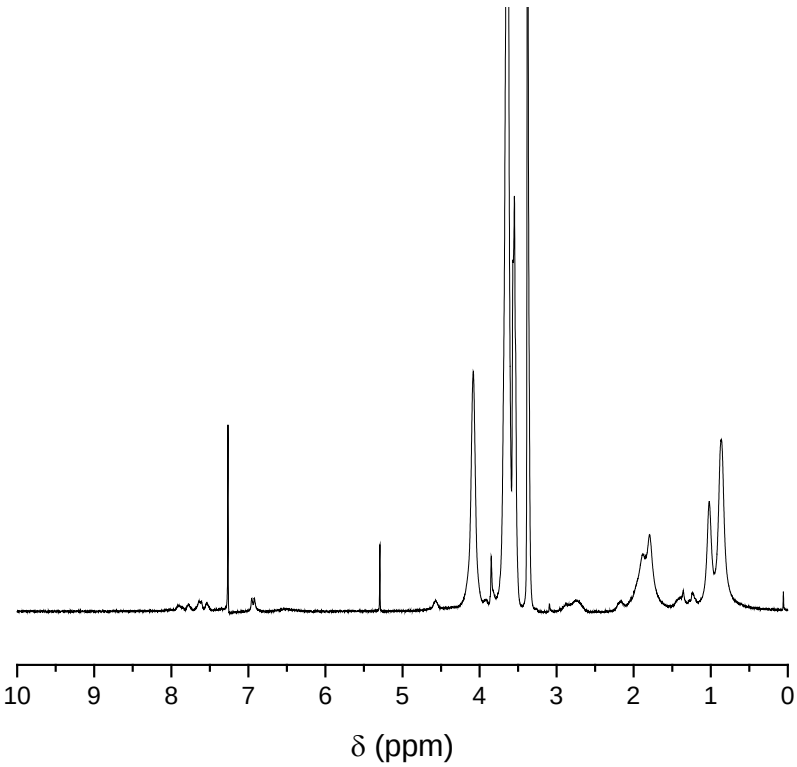


Figure 15. ^{1}H NMR (250 MHz, $CDCl_3$) of $\mathbf{P_R}$.

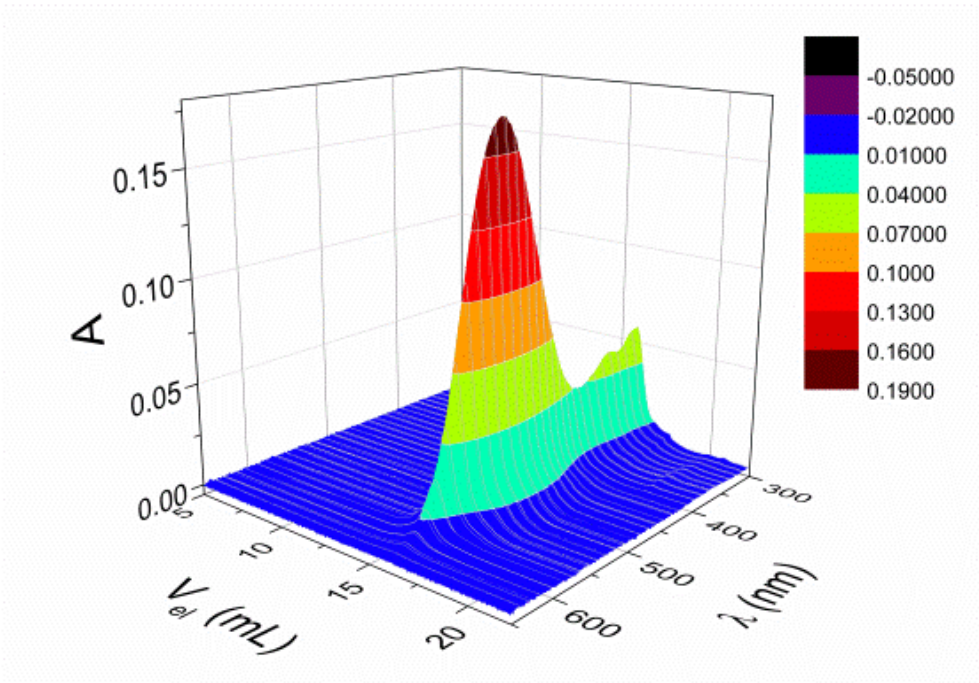


Figure 16. 2D-SEC (DMA, NH_4PF_6, PDA detector) of $\mathbf{P_R}$.

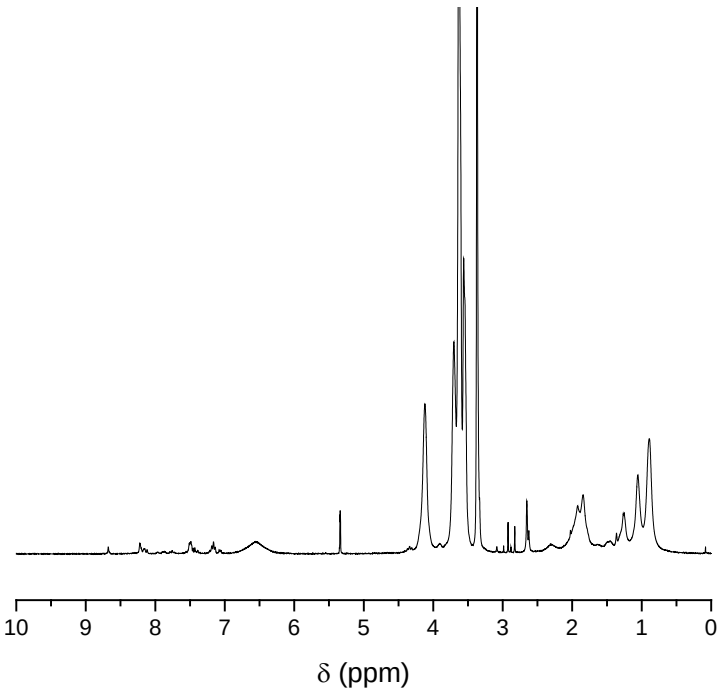


Figure 17. ^{1}H NMR (250 MHz, CD_2Cl_2) of $\mathbf{P_{Os}}$.

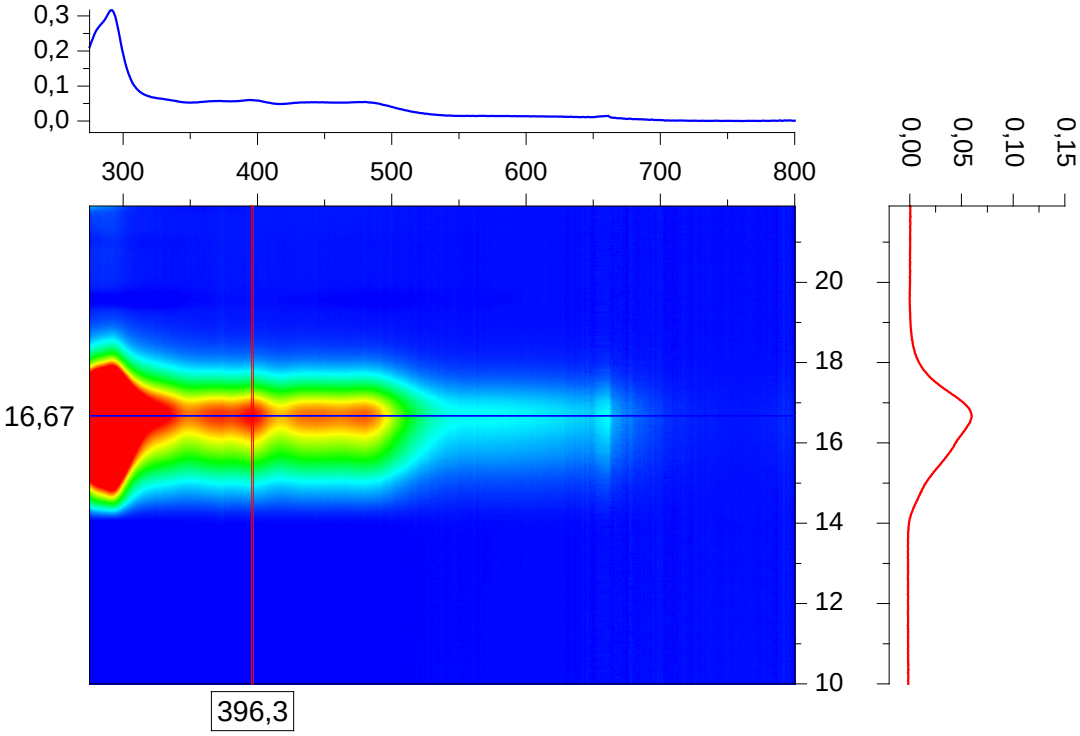


Figure 18. 2D-SEC (DMA, NH_4PF_6, PDA detector) of $\mathbf{P_{OS}}$.

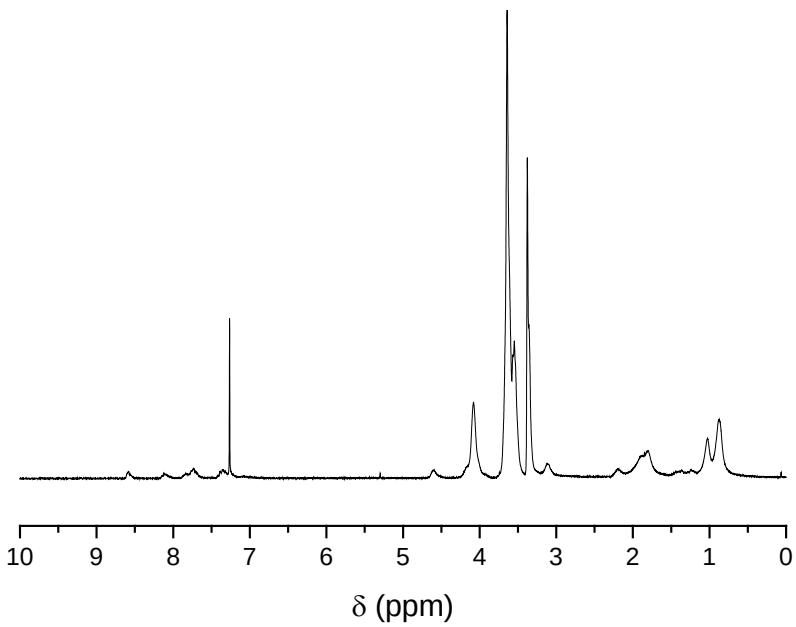


Figure 19. ^{1}H NMR (250 MHz, $CDCl_3$) of $\mathbf{P_{B\text{-}Y}}$.

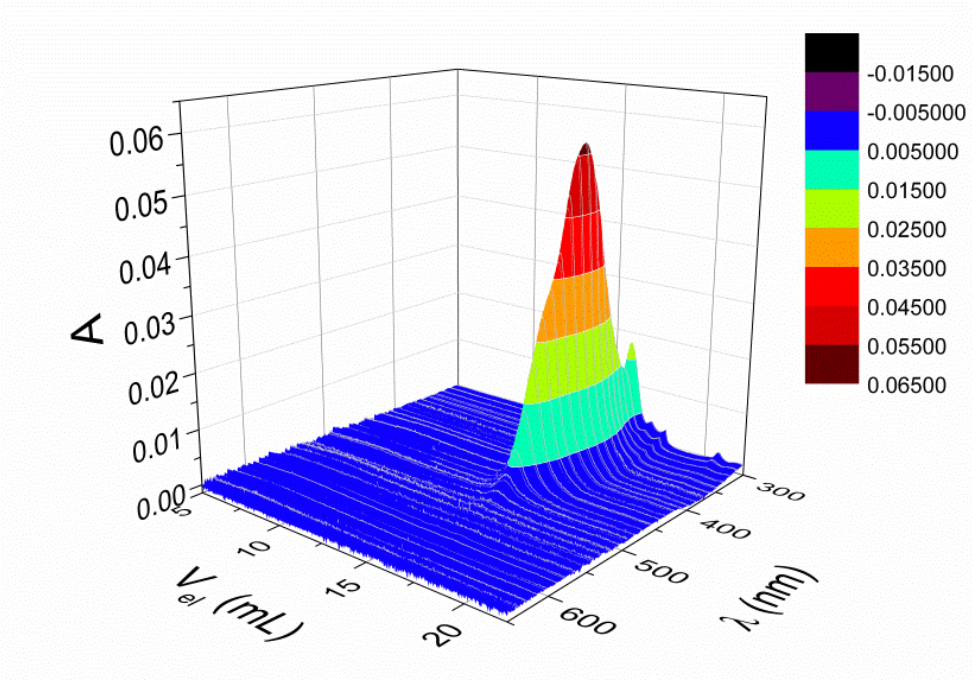


Figure 20. 2D-SEC (DMA, NH_4PF_6, PDA detector) of $\mathbf{P_{B\text{-}Y}}$.

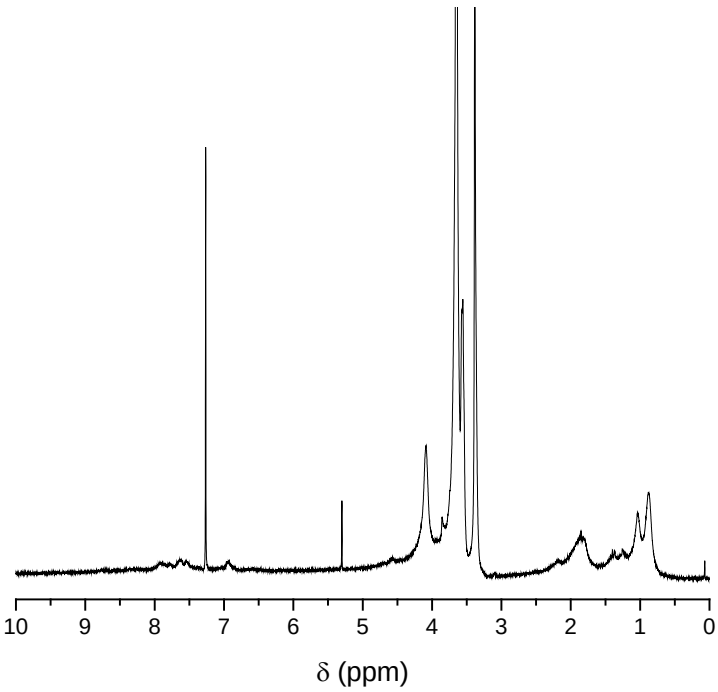


Figure 21. ^{1}H NMR (250 MHz, $CDCl_3$) of $\mathbf{P_{Y\text{-}R}}$.

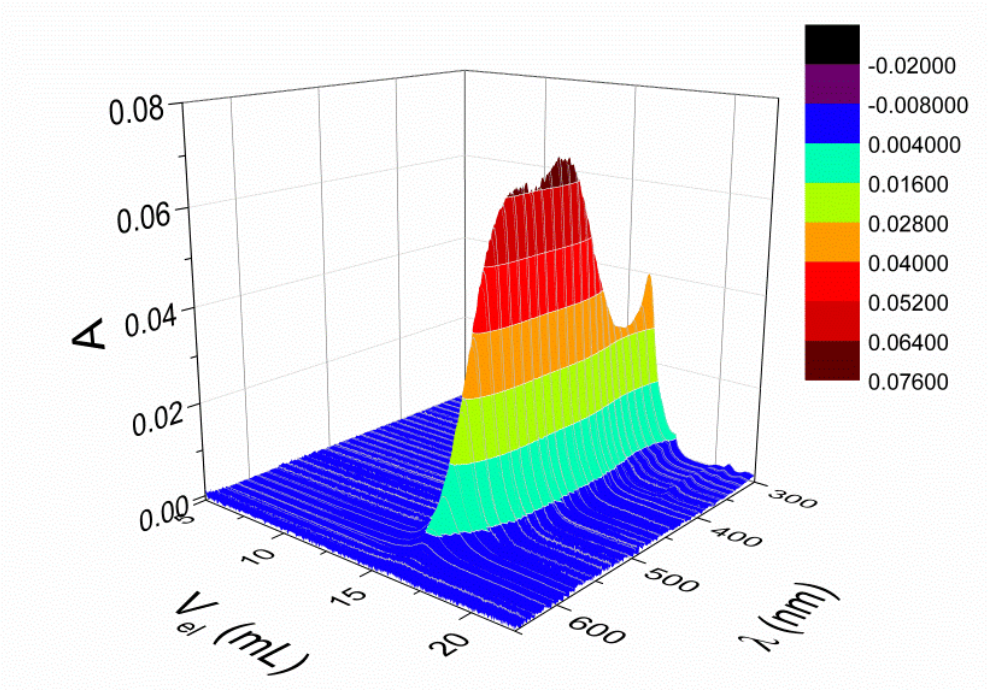


Figure 22. 2D-SEC (DMA, NH_4PF_6, PDA detector) of $\mathbf{P_{Y\text{-}R}}$.

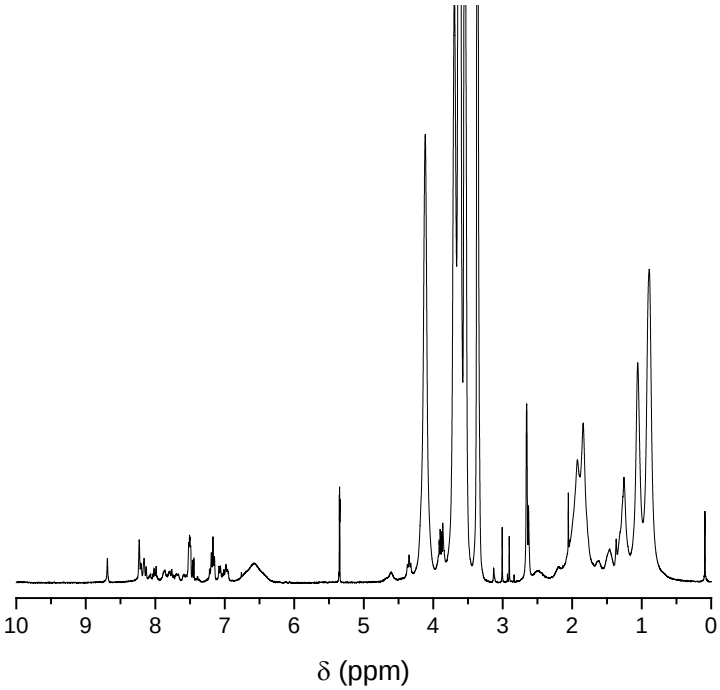


Figure 23. ^{1}H NMR (300 MHz, CD_2Cl_2) of $\mathbf{P_{R\text{-}Os}}$.

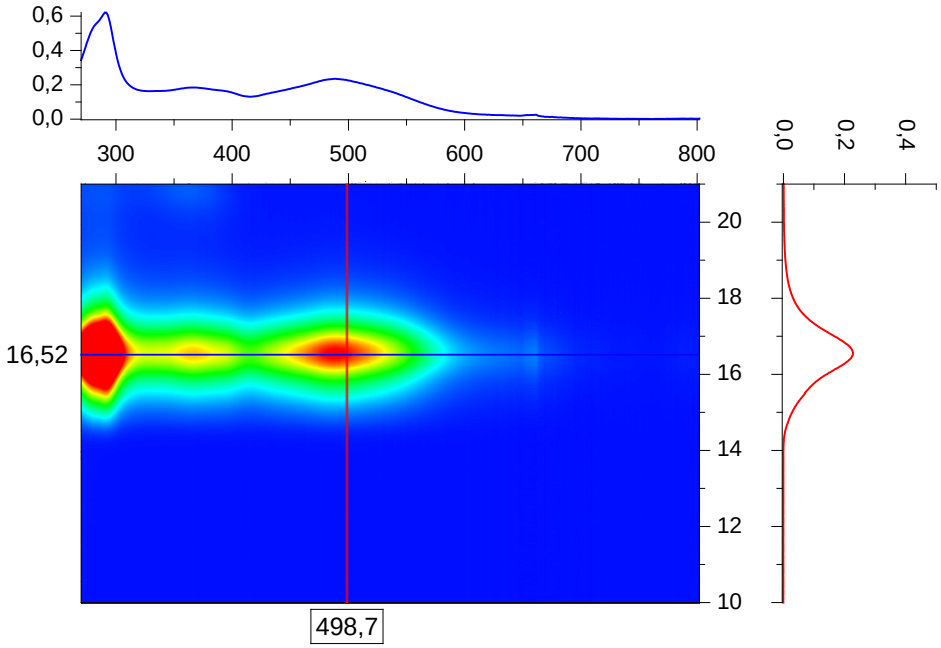


Figure 24. 2D-SEC (DMA, NH_4PF_6, PDA detector) of $\mathbf{P_{R\text{-}OS}}$.

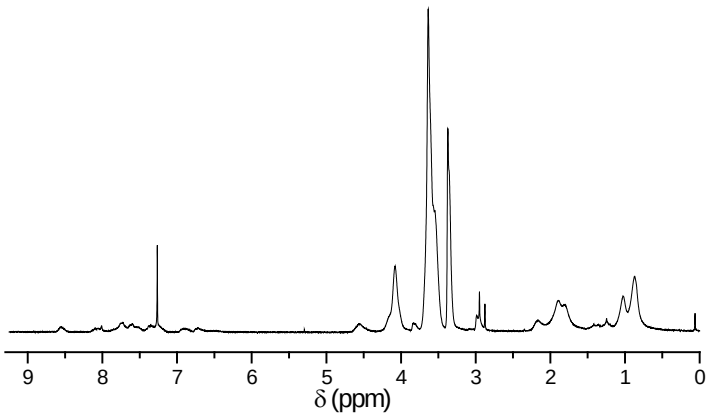


Figure 25. ^{1}H NMR (300 MHz, CD_2Cl_2) of $\mathbf{P_{B\text{-}Y\text{-}R}}$.

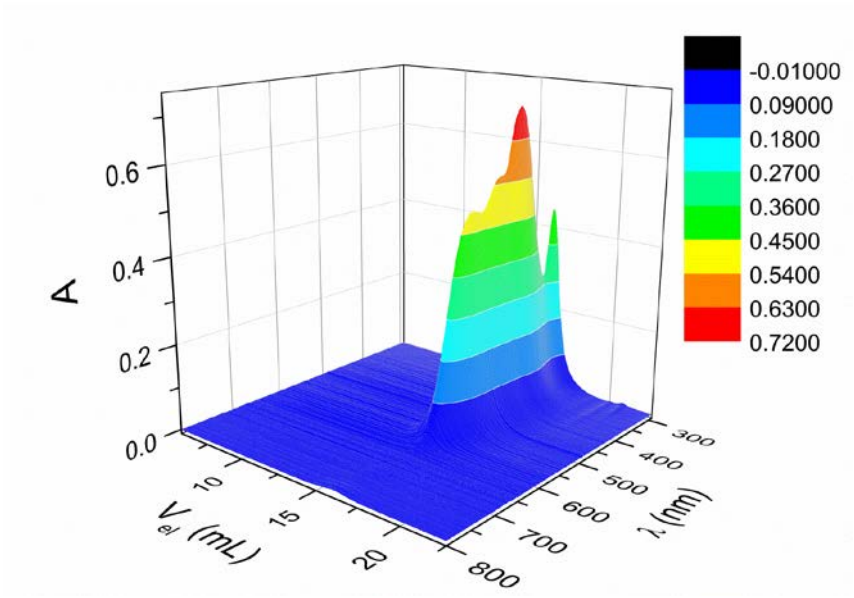


Figure 26. 2D-SEC (DMA, NH_4PF_6, PDA detector) of $\mathbf{P_{B\text{-}Y\text{-}R}}$.

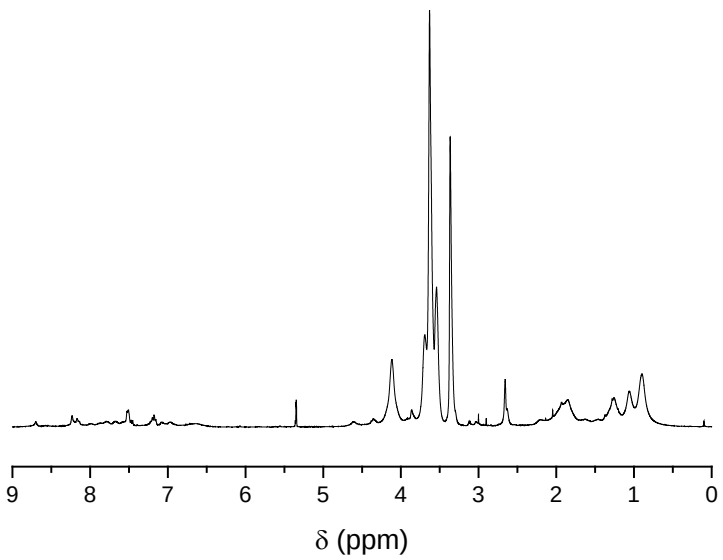


Figure 27. ^{1}H NMR (300 MHz, CD_2Cl_2) of $\mathbf{P_{Y\text{-}R\text{-}Os}}$.

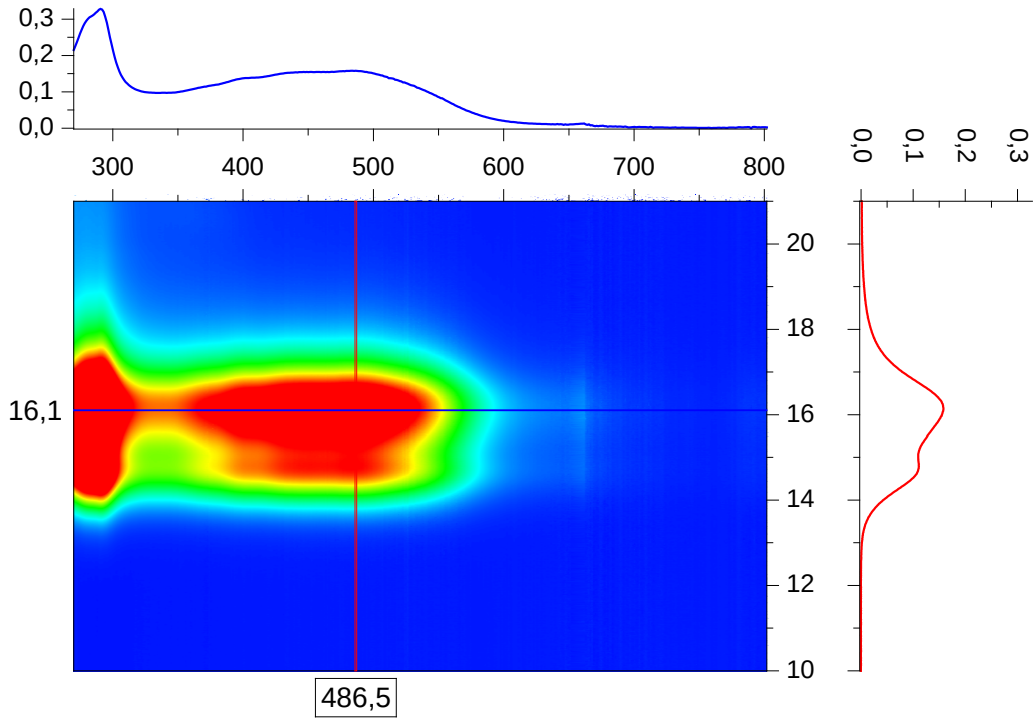


Figure 28. 2D-SEC (DMA, NH_4PF_6, PDA detector) of $\mathbf{P_{Y\text{-}R\text{-}OS}}$.

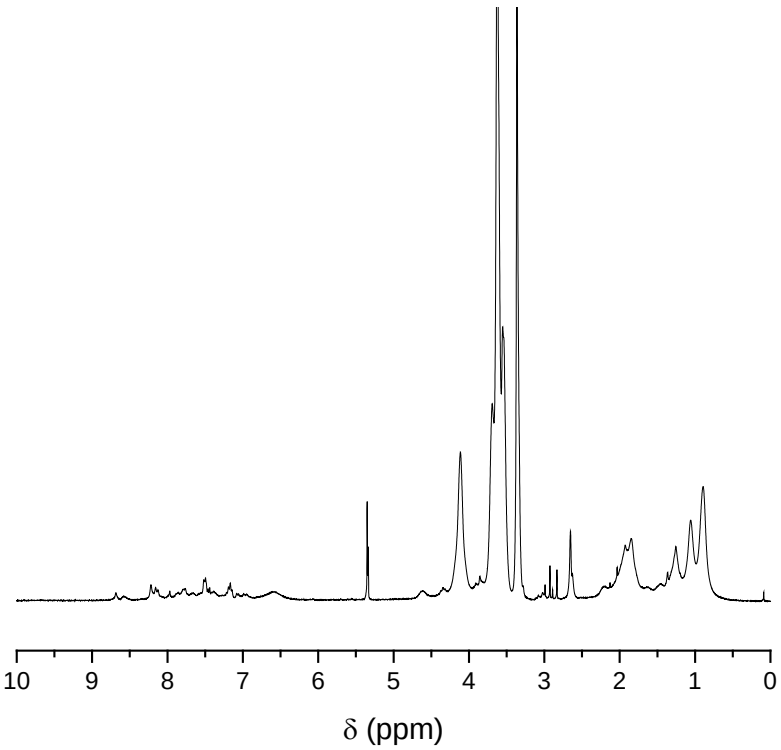


Figure 29. ^{1}H NMR (250 MHz, CD_2Cl_2) of $\mathbf{P_{B\text{-}Y\text{-}R\text{-}Os}}$.

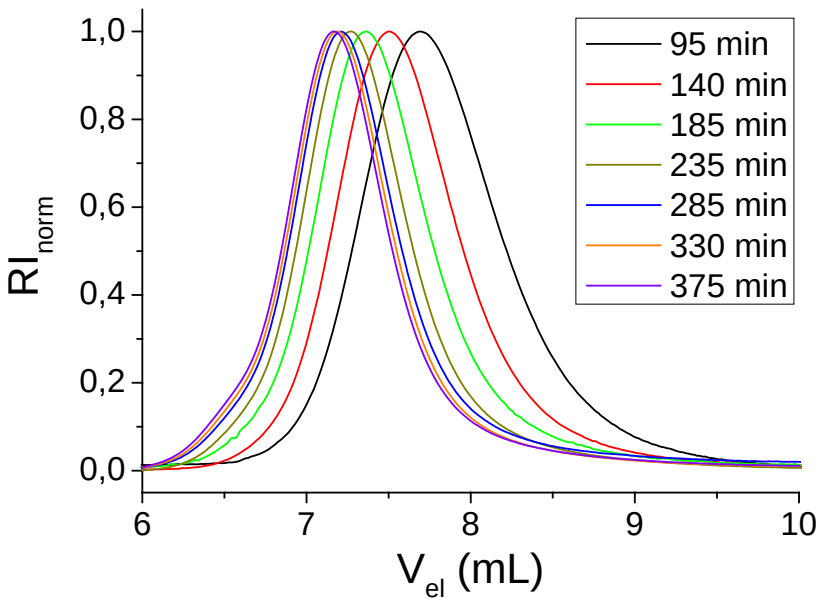


Figure 30. SEC ($CHCl_3$, RI detector) traces of the kinetic study for the polymerization of $\mathbf{P_B}$.

H_2-evolution

A photoactive Os(II) metal complex pendant polymer was tested for its performance as light harvesting assembly in an intermolecular system for visible light induced hydrogen formation.[3-4] $\mathbf{P_{Os}}$ was investigated as photosensitizer in an intermolecular system with colloidal platinum as catalyst for the reduction of protons to molecular hydrogen. For this purpose, $\mathbf{P_{Os}}$ was diluted in an acetonitrile/triethylamine/water (6/3/1) mixture (c_{Os} = 7×10^{-5} M). In this case, triethylamine acts as sacrificial electron donor. The colloidal platinum was *in situ* generated by the addition of K_2PtCl_4 (c = 7×10^{-5} M). Subsequently, the samples were irradiated at 470 nm using LEDs as light source. The hydrogen evolution was monitored by gas chromatography. **Figure 31** depicts the averaged absolute amounts of evolved hydrogen *versus* time plot. $\mathbf{P_{Os}}$ reveals only low H_2-production in the nmol scale. These values correspond to turn over numbers (TONs) of 0.85 (calculated by TON = $n_{Hydrogen}/n_{catalyst}$) in the

maximum at 6 h. These TONs below 1 display a hydrogen evolution below stoichiometric conversion relative the absolute content of Os(II) metal complex moieties. There was no more catalytic activity observed after 24 hours of irradiation. In comparison to other polymeric systems, the performance of our system at hand is situated below.[5] Nevertheless, the plot shows the potential for the application of antenna cascades for catalytic hydrogen evolution. Noteworthy, the structure of the Os(II)-metal complex is not optimized yet.

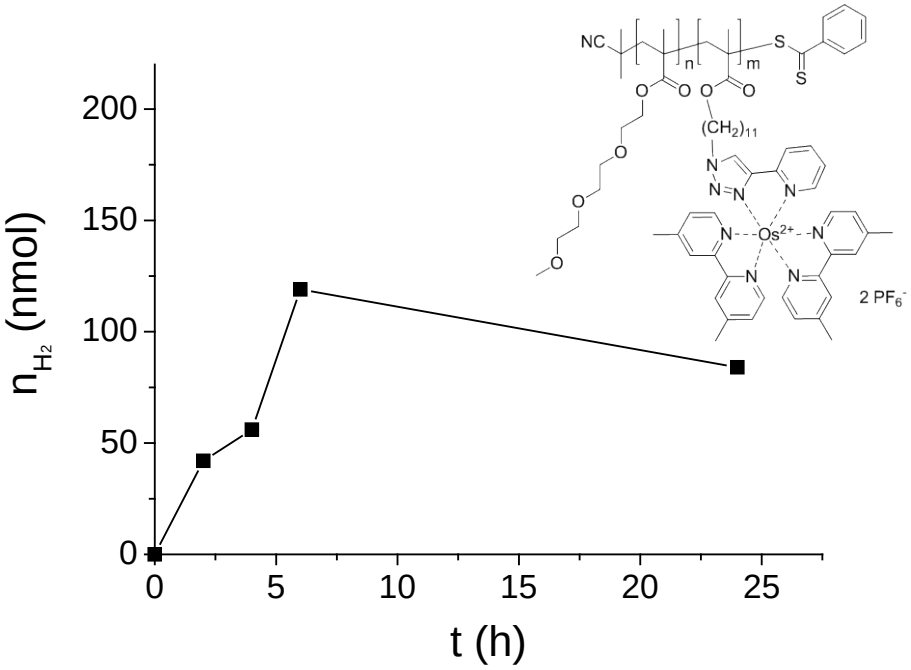


Figure 31. Hydrogen evolution of $\mathbf{P_{Os}}$ (n_{Os} = 0.14 µmol, n_{Os} corresponds to the absolute amount $\mathbf{M_{Os}}$ repeating units in the reaction mixtures) depending on the irradiation time in acetonitrile/triethylamine/water (6/3/1) with K_2PtCl_4 (c = 70 µM).

References

[1] R. Menzel, D. Ogermann, S. Kupfer, D. Weiss, H. Goerls, K. Kleinermanns, L. Gonzalez, R. Beckert, *Dyes Pigm.* **2012**, *94*, 512-524.

[2] A. M. Breul, J. Schaefer, E. Altuntas, M. D. Hager, A. Winter, B. Dietzek, J. Popp, U. S. Schubert, *J. Inorg. Organomet. Polym. Mater.* **2013**, *23*, 74-80.

[3] S. Tschierlei, M. Karnahl, M. Presselt, B. Dietzek, J. Guthmuller, L. Gonzalez, M. Schmitt, S. Rau, J. Popp, *Angew. Chem. Int. Ed.* **2010**, *49*, 3981-3984.

[4] S. Tschierlei, M. Presselt, C. Kuhnt, A. Yartsev, T. Pascher, V. Sundstroem, M. Karnahl, M. Schwalbe, B. Schaefer, S. Rau, M. Schmitt, B. Dietzek, J. Popp, *Chem. Eur. J.* **2009**, *15*, 7678-7688.

[5] K. Okeyoshi, R. Yoshida, *Soft Matter* **2009**, *5*, 4118-4123.